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THEORIES OF THE SORET EFFECT.

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It was observed in 1856 by Ludwig[1] and later independently by Soret[2] that, when two parts of a liquid solution are maintained at different temperatures, the solute will in general tend to migrate from the warmer to the colder region. The phenomenon has been the subject of several experimental researches.[3] The results obtained have not in general been in good agreement. This has no doubt been due to serious errors caused by convection, which is not easy to eliminate from a temperature gradient system : these errors will be considered in detail in a subsequent paper, but it may be mentioned here that they do not enter into the measurements made by Tanner[3] of the effect in concentrated electrolyte solutions, nor to any great extent into those of Wereide.[4] Unfortunately, Tanner's technique is not applicable to dilute solutions.

The first theory of the Soret effect was published in 1887 by Van't Hoff,[5] who extended the analogy between gases and dilute solutions to this effect and predicted that the solute would distribute itself so that its osmotic pressure was constant throughout the system. Since the osmotic pressure is given by

$$p = cRT,$$

where c is the concentration in mols per litre and R and T have their usual significance, the condition for Soret equilibrium according to this theory is that

$$cT = \text{constant},$$

or

$$\frac{d\ln C}{dT} = -1/T \qquad \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

The function $-\frac{d\ln C}{dT}$, is usually called the Soret coefficient and throughout this paper it will be denoted by σ.

The Van't Hoff theory then gives a value for σ of about -0.003 at ordinary temperatures. Van't Hoff found this to be in good agreement with Soret's value for $CuSO_4$ in aqueous solution, but the more accurate results of Tanner, extrapolated to infinite dilution, would give -0.012, a value four times as great. Moreover, the theory predicts the same value for all solutes in dilute solution, which a glance at the values obtained by Tanner will show to be a completely erroneous conclusion. The gas analogy is quite invalid, therefore, when applied to behaviour in a temperature gradient.

[1] *Wien. Akad. Ber.*, **20**, 539, 1856.
[2] *Arch. Genève*, **3**, 48, 1879 ; 4, 209, 1880. *Ann. Chim. Physique* (5) **22**, 293, 1881.
[3] Tanner, *Trans. Faraday Soc.*, **23**, 75, 1927, and other references there given.
[4] *Ann. Physique*, (9) **2**, 55, 1914.
[5] *Z. physik. Chem.*, **1**, 487, 1887.

Wereide,[4] employing kinetic theory methods, arrived at two possible formulæ, which may be re-written

$$\sigma = - 1/T \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad (2)$$

or

$$\sigma = - \frac{1}{2T} + \frac{1}{2} \frac{d \ln U}{dT} \qquad . \qquad . \qquad . \qquad . \quad (3)$$

Equation (2) will be seen to be the same as (1). In (3), U denotes the mobility of the diffusing molecule.

Porter,[6] using the same treatment as in the elementary theory of gas diffusion, arrived at the equation

$$c \sqrt{T} = \text{constant},$$

whence

$$\sigma = - \frac{1}{2T} \qquad . \qquad . \qquad . \qquad . \qquad . \quad (4)$$

Porter finds good agreement with the theory in the case of KI solutions, and introduces a factor dependent on the degree of ionisation to account for the deviations in the other cases. It seems improbable that the degree of ionisation could account for such enormous differences as actually exist, and the method is criticised by Chapman[7] as being quite inapplicable to liquid systems.

Chapman[8] has developed a kinetic theory which may be considered to replace these previous ones, because it is mathematically rigorous and the assumptions on which it rests are clearly stated. Chapman does not claim that his theory is applicable to any other solute than a colloidal suspension, and assumes that there is no unsymmetrical field of attractive forces acting on the particles. The conclusion arrived at is

$$cD = \text{constant} \qquad . \qquad . \qquad . \qquad . \quad (5)$$

where D is the diffusion coefficient. Assuming the validity of the Stokes-Einstein law, this may be re-written

$$c T/\eta = \text{constant},$$

where η is the viscosity of the suspending medium,

whence

$$\sigma = - 1/T + \frac{d \ln \eta}{dT} \qquad . \qquad . \qquad . \quad (6)$$

$$= - 0.026 \text{ at } 25° \text{ C. for water.}$$

Some experiments made by Dr. B. N. Ghosh and the author have demonstrated the existence of an effect in the direction indicated, in stannic oxide and ferric oxide hydrosols, but so far no quantitative results have been obtained.

If we attempt to apply the theory to molecular solutions it is best to employ the value for σ obtained directly from equation (5), namely

$$\sigma = - \frac{d \ln D}{dT} \qquad . \qquad . \qquad . \qquad . \quad (7)$$

This value is equal to exactly half that given by the second equation of Wereide, (3), but there can be no doubt that Chapman's derivation is more rigid. The values of the right-hand member of equation (7) for several electrolytes, taken from the work of Oholm,[9] are compared in Table I. with Tanner's figures for σ for the same substances at normal concentration.

[6] *Trans. Faraday Soc.*, **23**, 314, 1927.   [7] *Phil. Mag.*, **56**, 630, 1928.
[8] *Proc. Roy. Soc.*, **119A**, 34, 1928.   [9] *Z. physik. Chem.*, **50**, 309, 1904.

TABLE I.

Substance.	(Tanner.)	(Calc.)
K Cl	− 0·0009	− 0·0235
NaCl	0015	025
LiCl	0000	027
H Cl	0056	019
K O H	0118	021
NaO H	0122	023
Sugar	0014	028

It can be seen at once that there is very serious discrepancy. The calculated values are all too high, and the variation in them is not large, *i.e.*, they are only to a second order extent specific values, whereas the Soret coefficient is an entirely specific property of the substance. Moreover, the variations do not agree qualitatively, the three substances having the highest experimental values having also the lowest calculated ones. The theory, applied to molecular solutions, is therefore not only invalid, but is not even approximately valid.

In its extreme specificity the Soret effect more nearly resembles the solubility than any other property of the solute, and it is worth considering whether any connection can be traced. The mechanism of the phenomenon seems far too complicated for the kinetic theory to be a useful method of approach, and, since we are dealing with a distribution phenomenon, it seems probable that solubility will be a significant factor.

A substance will in general distribute itself between two phases of a liquid system in the ratio of its solubility in each. May this not also be true where the phases differ only infinitesimally in properties and are not separated by an interface, the property gradient being maintained by an external constraint?

In attempting to apply these ideas to the Soret effect, we are at once met by a difficulty. It is essential that the solubility measured in the different phases should be that of the substance in the same standard state. But where the phases differ in temperature this is impossible of achievement directly, since the pure substance must differ in temperature in the two measurements. The effect of temperature on the escaping tendency, or fugacity, of the pure solute must therefore be taken into consideration.

Let this fugacity be f_0 at the temperature T. Then at a temperature of $T + dT$ it will be $f_0\left(1 + \frac{d\ln f_0}{dT} . dT\right)$, and these will also be the values of the fugacity of the solute in solution at the saturation concentrations at these temperatures. Let these concentrations be C_s and $C_s\left(1 + \frac{d\ln C_s}{dT} . dT\right)$ respectively. Then the concentration which, at $T + dT$, has the same value, f_0, for the fugacity of the solute in solution as the concentration C_s at T, is

$$C_s\left(1 + \frac{d\ln C_s}{dT} . dT - \frac{d\ln f_0}{dT} . dT \middle/ \left(\frac{\partial \ln f_0}{\partial \ln C}\right)_T\right).$$

This is therefore the concentration at $T + dT$ which will be in equilibrium with C_s at T, if the solute distributes itself so that its fugacity throughout

the system is constant. The value for σ at the saturation concentration, which we will write σ_s, is therefore given by

$$\sigma_s = \frac{d\ln C_s}{dT} - \frac{d\ln f_0}{dT} \bigg/ \left(\frac{d\ln f}{d\ln C}\right)_T \qquad . \qquad . \qquad . \qquad (8)$$

This equation can be easily verified for the case of a volatile solute whose vapour pressure is small enough for it to be written directly equal to the fugacity. If we chose as standard state of the vapour that pressure which will give a constant concentration, *i.e.*, the vapour pressure over the solution at a given concentration, the first term of the right-hand side of equation (8) becomes zero, and we have

$$\sigma = - \left(\frac{\partial \ln p}{\partial T}\right)_C \bigg/ \left(\frac{\partial \ln p}{\partial \ln C}\right)_T \qquad . \qquad . \qquad . \qquad (9)$$

Making use of the figures for the vapour pressure of HCl over aqueous solutions obtained by Weisberg,[10] the value for σ for normal HCl solution at 33° C. given by equation (9) is $- 0.045$, which is numerically about eight times as great as the experimental value of Tanner. We must conclude therefore that the solute does not distribute itself so that its fugacity is constant.

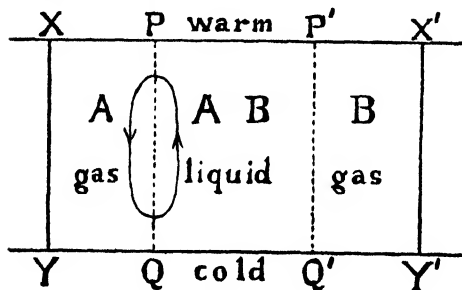The reason for this becomes clear on reference to the system represented diagrammatically in Fig. 1. XX', YY' are horizontal plates maintained at different temperatures, the upper one being the hotter. The central compartment of the space between the plates contains the liquid solution of B in A, and its boundary walls are membranes, PQ being permeable only to the vapour of A and P'Q' only to that of B. XY, X'Y', are solid walls and the outer compartments XYQP, P'Q'Y'X', contain only vapour of A and B respectively.

Fig. 1.

The condition that B distributes itself to constant fugacity means that the vapour pressure of B will be everywhere the same, *i.e.*, that there will be no cyclic flow of B in the system PQY'X'. Since the vapour pressure increases with the temperature and also with the concentration of B, the concentration of B must increase with decreasing temperature, for this condition of no flow in PQY'X' to be fulfilled.

Now consider the system XYQ'P'. The vapour pressure of A will increase with increasing temperature and with decreasing concentration of B, both of which factors act in the same direction, so that the movement of B which brings that component to constant fugacity will increase the gradient of fugacity of A. In this part of the system therefore the vapour pressure of A in the upper part will be greater than that in the lower part, and there will be a cyclic flow of A in the direction indicated by the arrow.

It is therefore impossible for cyclic flow to be eliminated from the system, *i.e.*, both components cannot be in thermodynamic equilibrium, and it remains to be considered whether this can be in general true of either. There are many examples of systems treated thermodynamically where one component only is in true equilibrium, but in all these the other components are either constrained by semipermeable membranes or by

[10] Landolt and Bornstein, "*Tabellen,*" E., p. 760.

being not appreciably volatile. The classical system for the demonstration of the connection between osmotic pressure and lowering of vapour pressure is such an example: here we are dealing with equilibrium in the solvent only: the solute is constrained by the osmotic membrane, and, if it is appreciably volatile, another semipermeable membrane must be introduced. In the temperature gradient case, however, both components are free, and the distinction between solvent and solute is a purely arbitrary one. There seems no reason to assume that either will be peculiarly favoured. The system may best be described as being in a state of thermodynamic strain, the condition being maintained at the expense of a constant entropy increase of the whole system (including the temperature reservoirs).

An analogous system, in which the gradient of property is maintained under isothermal conditions by the diffusion of a third component, is described in another paper,[11] and in this case there may be an *apparent* equilibrium of one only of the stationary components, where its concentration is very small and its activity very greatly influenced by the third component. There may be also a simple relation between the activity gradients of the two stationary components, as both are due to a kinetic effect. Neither of these simplifications however is true of the temperature gradient case because the gradient of temperature will strain both components to comparable extent, and the mechanism of the gradient is intimately linked up with the nature of the attractive forces. We must conclude that there is in general no simple relationship between the strains in the components in the temperature gradient case, and therefore that the phenomenon is incapable of treatment by use only of the ordinary thermodynamic functions.

The impossibility of thermodynamic equilibrium in the system of Fig. 1 is at once realised by consideration of a one-component system. This consideration is also instructive when applied to Chapman's theory. Cohen and Bruins [12] have shown that the Stokes-Einstein law for diffusion is approximately valid even for self-diffusion in perfect liquids. The same mathematical treatment is used in the derivation of this law as in that of Chapman's formula, and one might therefore at first expect the latter also to be applicable to a pure liquid. Suppose that a small fraction of the molecules of the liquid are marked in some way which does not alter their behaviour: these may be considered as a dilute solution in the others, and we should therefore, by (6), expect them to show a Soret effect of magnitude

$$\sigma = -\ 1/T + \frac{d ln \eta}{dT}$$

but as there is no real distinction between the marked and unmarked molecules, this formula must also be applicable to the whole liquid, and as the volume concentration of this latter is proportional to the density ρ, we may write

$$\frac{d ln \rho}{dT} = -\ 1/T + \frac{d ln \eta}{dT}.$$

For all liquids the last term is negative, and the interpretation of the equation is therefore that liquids will have coefficients of thermal expansion considerably greater than that of a perfect gas, instead of, as is actually the case, considerably less.

The common error of all the theories so far described is that they attribute to the solvent no other rôle than that of a vehicle or carrier of

[11] See p. 10.   [12] *Z. physik. Chem.*, **103**, 404, 1923.

the solute.   But actually the solvent molecules have a tendency to migrate from the warmer to the colder region also, and the Soret effect is a result of a balance between the two tendencies.   And so the attractive forces, which can be neglected in the Stokes-Einstein treatment of isothermal diffusion because they neutralise one another, become of paramount importance in the mechanism of the Soret effect.

The cyclic movement in Fig. 1 is strongly suggestive of the electric thermo-couple.   Electrolytic thermo-couples have long been known and have been the subject of several researches.[13]   A theory was advanced by Eastman,[14] in 1926, connecting the " homogeneous effect " in these couples with the Soret effect in electrolytes, and has been further developed by the same author[15] and in a very exhaustive treatise by Wagner.[16]

The fundamental concept of the Eastman theory is that of " heat of transfer," denoted by Q^* and defined as the quantity of heat absorbed by a mol of diffusing substance, in an infinite solution, from the region which it leaves, and given out again to the region to which it diffuses.   The quotient of Q^* by T is the corresponding " entropy of transfer " and is denoted by S^*.   These quantities differ from all ordinary thermo-dynamic functions in referring to changes within a single phase rather than to exchanges between phases.   It is questionable whether they can be considered reversible functions, and Eastman divides them into two parts denoted respectively reversible and irreversible: he considers, however, that the irreversible part is negligible in the case of liquid solutions.

The equation arrived at by Eastman for the Soret effect is

$$\left(\frac{\partial \overline{F_A}}{\partial N_A}\right)_{p,\,T} . \, dN_A = - \, Q_A^* / T \, . \, dT$$

$$= - \, S_A^* \, . \, dT.$$

where $\overline{F_A}$ is the partial molal free energy of component A, and N_A its mol fraction.

This may be expressed

$$\left(\frac{\partial \overline{F_A}}{\partial N_A}\right)_{p,\,T} \left(\frac{\partial N_A}{\partial T}\right)_{soret} = - \, S_A^* \qquad . \qquad . \qquad . \quad (10)$$

or

$$\left(\frac{\partial \overline{F_A}}{\partial ln N_A}\right)_{p,\,T} \left(\frac{\partial ln N_A}{\partial T}\right)_{soret} = - \, S_A^* \qquad . \qquad . \qquad . \quad (11)$$

The function $\left(\dfrac{\partial \overline{F_A}}{\partial ln N_A}\right)_{p,\,T} . \left(\dfrac{\partial ln N_A}{\partial T}\right)_{soret}$ is called by Eastman the

" thermodynamic soret coefficient."   In dilute solutions $\left(\dfrac{d \overline{F_A}}{\partial ln N_A}\right)_{p,\,T}$

becomes equal to RT and equation (11) may be rewritten

$$RT\sigma = - \, S_A^* \qquad . \qquad . \qquad , \qquad . \qquad . \quad (12)$$

Applying to this theory the test, namely interchangeability of solvent and solute, which proved the fallacy of the previous theories, we have, for a system A-B, equation (10) for the component A, and we may derive from this the corresponding equation for B as follows.   By the fundamental equation for partial molal quantities,

[13] See references in Wagner's paper.   [14] *J. Am. Chem. Soc.*, **48**, 1482, 1926.
[15] *Ibid.*, **50**, 283, 1928.   [16] *Wied. Ann.* (5) **3**, 629, 1929.

$$N_A d\bar{F}_A + N_B d\bar{F}_B = 0,$$

whence
$$d\bar{F}_A = -\frac{N_B}{N_A}.d\bar{F}_B$$

and, since $N_A + N_B = 1$, $\qquad dN_A = -dN_B$,

further, since diffusion of one mol of A from region 1 to region 2 produces the same infinitesimal concentration changes as diffusion of N_B/N_A mols of B from region 2 to region 1.

$$S_A^* = -\frac{N_B}{N_A}.S_B^*.$$

Substituting these values in equation (10) we obtain

$$\left(\frac{\partial \bar{F}_B}{\partial N_B}\right)_{p,\,T}\left(\frac{\partial N_B}{\partial T}\right)_{soret} = -S_B^*$$

which is seen to be the same as (10) with suffix B for suffix A. The theory is thus consistently applicable to both components.

For solutions of electrolytes, Q^* and S^* are replaced by the sum of the corresponding quantities for the two ions. The theory, therefore, predicts that, as long as the quantities for cation and anion are independent of one another, the Soret coefficient will be an additive property of the ions. This is not borne out, or only in a qualitative way, by Tanner's values. It may, however, be true in very dilute solution. The heat and entropy of transfer of ions must therefore vary very much more with concentration and the presence of other ions than the mobility, since the conductivity of electrolytes is an approximately additive phenomenon at fairly considerable concentrations.

Eastman's equation for the *homogeneous E.M.F.*, *i.e.*, the *E.M.F.* gradient set up in a homogeneous solution when it is subjected to a temperature gradient, before an appreciable concentration gradient has been established, is

$$F.\frac{dE}{dT} = t_C.S_C^* - t_A.S_A^* \qquad . \qquad . \qquad . \quad (13)$$

where F is the equivalent of electricity and t_C, t_A are the transport numbers of cation and anion respectively.

Using the data of Podszus, and making certain very plausible assumptions, Eastman was able to compile a provisional table for the entropies of transfer of some of the commoner ions, and applied these to the data of Richards[17] for the *E.M.F.* of calomel electrode thermocells, in order to calculate the partial molal entropy of the chloride ion. His values for this quantity were satisfactorily constant. Wagner[16] criticises Eastman's neglect of the *homogeneous E.M.F.* for water.

It is doubtful whether the heat of transfer as defined by Eastman will be independent of the mechanism of transfer, whether it be free diffusion or movement in an electric field. Eastman assumes that the molecule diffusing leaves behind it molecules that were previously bound, but which must now take up their quota of kinetic energy from the surroundings, thereby absorbing heat. This mechanism would seem to depend on whether the molecule is drawn forward by an external force, or pushed forward by the surrounding molecules. The same argument might be levelled against the Nernst theory of diffusion in electrolytes, and be met by the excellent agreement of the theory with experiment,[18] but the fact

[17] *Z. physik. Chem.*, **24**, 39, 1897. [18] Oholm, *Z. physik. Chem.*, **50**, 309, 1904.

that the mobility is independent of the nature of the applied force does not necessarily mean that this is also true of the energy relationships. It was shown [19] that, in the case of the composition gradient, the effect indicated by Chapman's formula, *i.e.*, the tendency of the molecules to move from the region of higher to that of lower diffusion velocity, does not exist independently of the "solubility effect." This suggests that the former must be included in the latter, *i.e.*, that the factors leading to decrease of the diffusion velocity must also lead to an increase of solubility. We should expect therefore that, in the case of the Soret effect too, the thermo-dynamic theory must automatically include these factors. Eastman assumes that when attractive forces cease to operate, Q^*, and therefore the Soret effect, must be zero : it is just in this limiting case, however, that we should expect Chapman's theory to become valid, which would mean a very large Soret effect. It would seem, therefore, that Eastman's theory does not include the factors dealt with by Chapman. In view of these doubts it is interesting to derive the connection between the Soret effect and *homogeneous thermal E.M.F.* in electrolytes from more general considerations.

In ordinary diffusion processes, the diffusing substance may be considered as moving under the influence of a uniform pressure against the viscous resistance of the solvent. This pressure is equal to the gradient of osmotic pressure. As was shown in the composition gradient case,[20] this is not in general true where there is a gradient of property, since at the equilibrium gradient there may still exist a finite osmotic pressure gradient. This latter must be considered as neutralised at equilibrium by the internal forces of the system. For any other gradient, therefore, the driving force will be numerically equal to the gradient of osmotic pressure less the value of this in the equilibrium gradient. Expressed in terms of the activity α this gives

$$- P = RT \frac{d\alpha}{dh} - RT \left(\frac{d\alpha}{dh}\right)_e \qquad . \qquad . \qquad . \quad (14)$$

where the suffix e denotes equilibrium between the statistical effect and internal forces, and P is the resultant driving force on the diffusing component contained in unit volume of the solution. Where there exists a temperature gradient dT/dh, the terms on the right-hand side of (14) may be split up as follows

$$\frac{d\alpha}{dh} = \left(\frac{\partial \alpha}{\partial T}\right)_C \cdot \frac{dT}{dh} + \left(\frac{\partial \alpha}{\partial C}\right)_T \cdot \frac{dC}{dh}$$

and

$$\left(\frac{d\alpha}{dh}\right)_e = \left(\frac{\partial \alpha}{\partial T}\right)_C \cdot \frac{dT}{dh} + \left(\frac{\partial \alpha}{\partial C}\right)_T \cdot \left(\frac{dC}{dh}\right)_e.$$

Adding these, the effects due to temperature alone cancel out and we have

$$- P = RT \cdot \left(\frac{\partial \alpha}{\partial C}\right)_T \left[\frac{dC}{dh} - \left(\frac{dC}{dh}\right)_e\right]. \qquad . \qquad . \quad (15)$$

Dividing throughout by dT/dh and writing, since we are dealing only with very dilute solutions, $\left(\frac{\partial \alpha}{\partial C}\right)_T = 1$, the equation becomes

$$- \left(\frac{dh}{dT}\right) P = RT \cdot \left[\frac{dC}{dT} - \left(\frac{dC}{dT}\right)_e\right]. \qquad . \qquad . \quad (16)$$

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[19] *See* following paper.   [20] *See* p. 13.

To obtain the driving force per mol of solute, we must divide throughout by C, whence

$$- \left(\frac{dh}{dT}\right)\frac{P}{C} = RT \cdot \left[\frac{dlnC}{dT} - \left(\frac{dlnC}{dT}\right)_e\right] \qquad . \qquad . \quad (17)$$

In the case of electrolytes we shall use suffixes $+$ and $-$ to refer to the cation and anion respectively. There will be additional forces on the ions due to the electric field dE/dT. $\left(\frac{dlnC}{dT}\right)_{e,+}$ and $\left(\frac{dlnC}{dT}\right)_{e,-}$ will not then in general be the same. They represent the logarithmic gradients of concentration in which the ion in question is subjected to electric forces only, the statistical effect and internal forces cancelling one another. It seems probable that these will, in dilute solution, be specific properties of the ion concerned. We shall denote them by σ_+ and σ_-. The values for the resultant forces on the ions will therefore be

$$- F \cdot \frac{dE}{dT} - RT\frac{dlnC}{dT} + RT\sigma_+ \qquad . \qquad . \qquad . \quad (18)$$

and

$$+ F \cdot \frac{dE}{dT} - RT\frac{dlnC}{dT} + RT\sigma_- \qquad . \qquad . \qquad . \quad (19)$$

For Soret equilibrium, there is no movement of either ion, so that in this case both (18) and (19) will be zero, and $\frac{dlnC}{dT}$ becomes equal to the Soret coefficient σ, whence we have, by addition,

$$\sigma = \tfrac{1}{2}(\sigma_+ + \sigma_-) \qquad . \qquad . \qquad . \qquad . \quad (20)$$

and, by subtraction,
$$F \cdot \frac{dE}{dT} = \frac{RT}{2}(\sigma_+ - \sigma_-) \qquad . \qquad . \qquad . \qquad . \quad (21)$$

For the homogeneous condition, before appreciable diffusion has taken place, we have, for the velocity of transfer of the ions, since $dlnc/dT = 0$.

$$\left(- F \cdot \frac{dE}{dT} + RT \cdot \sigma_+\right) \cdot u \qquad . \qquad . \qquad . \quad (22)$$

$$\left(+ F \cdot \frac{dE}{dT} + RT \cdot \sigma_-\right) \cdot v \qquad . \qquad . \qquad . \quad (23)$$

where u and v are the mobilities of the ions. Since there can be no appreciable separation of the ions during diffusion, (22) and (23) must be equal, whence

$$F \cdot \frac{dE}{dT} = \frac{RT}{u + v}(u\sigma_+ - v\sigma_-) \qquad . \qquad . \qquad . \quad (24)$$

The equations (20), (21) and (24) are identical with the corresponding equations derived from Eastman's theory, if we write, on analogy with equation (12)

$$RT\sigma_+ = - S_C^* \qquad . \qquad . \qquad . \qquad . \quad (25)$$

and
$$RT\sigma_- = - S_A^* \qquad . \qquad . \qquad . \qquad . \quad (26)$$

The fundamental assumption in this treatment is the same as that in the Nernst treatment of isothermal diffusion in electrolytes, namely that a gradient of osmotic pressure produces the same velocity of ion transfer as an electric field which gives rise to the same force per ion. The assumption of the Eastman theory is that these two causes give rise to the same energy transfers.

The identity of the two conclusions is strong evidence that the one assumption is consequent on the other, and, as the first is verified in the case of dilute solutions by the independent evidence of the study of iso-thermal diffusion, this must also give support to Eastman's assumption.

No reliable figures are available for the Soret effect in dilute solutions, but it will be seen from a consideration of Tanner's values that the additivity predicted is only very roughly true for concentrated solutions. It seems, therefore, that the Eastman theory of the Soret effect has a more limited applicability than the Nernst diffusion theory. It should be noticed, however, that the minor assumption on which the additivity conclusion rests, namely that σ_+ and σ_-, or S_A^* and S_C^*, are themselves constant in dilute solution, is really independent of the major assumptions above discussed. We must conclude that these functions depart rapidly from constancy as concentration is increased.

Summary.

Various kinetic theories of the Soret effect have been reviewed, and the error common to them pointed out.

The impossibility of there being any valid theory which makes use only of standard thermo-dynamic functions has been demonstrated.

Independent support has been obtained for the conclusions of Eastman's theory.

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DIFFUSION AND DISTRIBUTION IN A SOLVENT OF GRADED COMPOSITION.

BY G. S. HARTLEY.

It was shown in the previous paper that, while the Stokes-Einstein law is approximately valid for the diffusion of an ordinary molecular solute, Chapman's treatment on the same mathematical principles of the distribution of particles suspended in a medium of graded properties, is quite invalid when the particles are of molecular size and the property concerned is the temperature of the system.

The object of the research described in this paper was to examine the distribution of a molecular solute in a solvent having a gradient of some other property, namely a gradient of concentration of a second solute.

Application of Chapman's formula would lead us to expect that the first solute will distribute itself in the inverse ratio of its diffusion constant in the layers of solvent of different composition.

Application of the distribution considerations outlined in the previous paper would lead us to expect that the first solute will distribute itself in the ratio of its solubility in the various layers.

If, however, we consider the system in Fig. 1, we find that the second of these theoretical approaches involves the same complication that was

met with in the temperature gradient case. It ignores the equilibrium of the solvent.

XX′, YY′ are membranes permeable only to the second solute, C. XY is permeable only to the first solute, B, and X′Y′ only to the solvent, A. The space above XX′ is a large reservoir of vapour of C at a pressure $p + dp$, and that below YY′ a large reservoir of vapour of C at pressure p. A constant gradient of concentration of C is thus maintained across the liquid solution in the middle compartment. If the fixed solute, B, distributes itself in the ratio of its solubility in the various concentrations of the A-C solution, there will be no circulation of vapour in the B compartment. It is obvious that this condition of no circulation cannot in general be also true of the A compartment, for, at the greater concentration of C, the vapour pressure of A will be less than at the smaller, and the movement of B in the solution will not necessarily be in the right sense to compensate for this effect. Again, the concentration of B may be so much less than that of C that any movement in it will be wholly inadequate to compensate for the effect of C on the vapour pressure of A. In the limit, B may be removed altogether, and we are left with a gradient of fugacity in the static substance A consequent on that in the diffusing substance, C. The static components will in general then be in a state of thermo-dynamic strain, and it is clear that it is the constant degradation of energy in the diffusion of the free component which maintains this strain.

A mechanical interpretation of this phenomenon must be somewhat as follows. In consequence of the gradient of concentration of the component C, it has also a gradient of osmotic pressure. This is the driving force that causes its diffusion. This driving force may also be regarded as pushing the static components back, thus building up a

Fig. 1.

gradient of diffusion pressure in them in the reverse sense to its own gradient. We should expect from this argument that the gradients of diffusion pressure in the static components will be in the same sense.

The larger molecules among those of the static components will be subjected to greater bombardment by the diffusing molecules than will the smaller ones, the pressure thus exerted on them being approximately proportional to their mean area. But all the molecules will have on the average the same kinetic energy, and, for the same logarithmic concentration gradient, can be considered as subject to the influence of the same osmotic pressure gradient. The static components with larger molecules will, therefore, require a greater logarithmic concentration gradient than those with smaller ones, when subjected to the pressure of the same diffusing molecules.

This leads to the conclusion that the gradient of diffusion pressure in the same system will be, for each static component, proportional to the mean cross-sectional area of its molecules in solution, i.e., since the
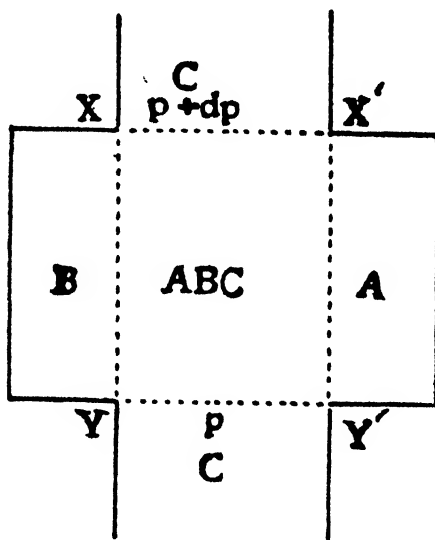
diffusion constant is inversely proportional to the molecular radius, inversely proportional to the square of its diffusion constant.

It is obvious that this diffusion "push" effect must be taken into account also in the application of Chapman's formula, and will lead to the values predicted for the concentrations of the static solute at different compositions of the solvent needing a correction in the sense that those for low concencentrations of the diffusing solute must be increased and those for higher concentrations diminished.

In the above discussion, the words "diffusion pressure" have been used in place of "osmotic pressure" because there is evidence to show that in a graded system the gradients of the two are not the same. A component may have twice the concentration, and hence twice the osmotic pressure, in one part of the system as it has in another, and yet show no tendency to diffuse from the former to the latter part because it is twice as soluble in the solvent in the former as in the latter part.

The work of Öholm[1] has shown that, if we make allowance in the diffusion of electrolytes for the non-linear variation of osmotic pressure with concentration, we obtain a constant value for the diffusion constant up to nearly normal concentrations. This can be done by substituting the individual activities for the concentration of the ions in the Nernst[2] treatment of electrolyte diffusion. We then obtain for the molar rate of transfer per unit cross-section of the diffusing column, for a gradient of concentration $\frac{dc}{dh}$,

$$ V = - RT \cdot \frac{UV}{U + V}\left(\frac{d\alpha_+}{dh} + \frac{d\alpha_-}{dh}\right) $$

where α_+ and α_- are the activities of the cation and anion respectively at concentration c. The activity here is defined by $\alpha = c$ for $c = 0$. This equation may be rewritten

$$ V = - \frac{UV}{U + V} \cdot \frac{dp}{dh} $$

where p is the osmotic pressure of the electrolyte, and is therefore verified by Öholm's results. If we write $D' = RT\frac{UV}{U + V}$, this being equal to the diffusion constant as ordinarily defined at infinite dilution, and replace α_+ and α_- by their arithmetic mean, α, we can write the differential form of Fick's equation as

$$ \frac{dC}{dt} = - D' \cdot \frac{d^2\alpha}{dh^2} . \qquad . \qquad . \qquad . \qquad . \quad (1) $$

in which form the diffusion constant is independent of concentration in moderately dilute solutions.

Can we now, by referring the activity to some standard state of the pure solute, develop an equation which will be valid for the graded solvent? This is difficult for the case of an electrolyte, because, if we make the activity unity in the saturated solution, whatever the composition of the solvent, we are using the activity of the undissociated solute, i.e., the product of the individual ion activities and not their mean. The treatment is simple, however, for the case of an undissociated solute.

Let α as before denote the activity defined by $\alpha = c$ at infinite dilution. Let α_s be the value of α in the saturated solution at any

[1] Z. physikal. Chem., 50, 309, 1904.   [2] Ibid., 2, 613, 1888.

composition of solvent. α_s will be of course a function of this composition. Let β be the activity defined with reference to that of the solid solute as unity : then $\beta_s = 1$ for all compositions of solvent, and, since α and β are proportional at any given composition,

$$\alpha = \beta \cdot \alpha_s \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

If there were no "push" effect from the diffusing components, we should expect the solute to distribute itself so that β is constant throughout the system. We should, therefore, expect that the velocity of diffusion will be governed by the gradient of β and not α. If we substitute β for α in the modified form of Fick's equation, however, we must alter the value of the diffusion constant. To determine this value, consider the case of diffusion in a homogeneous solvent, and write $\beta\alpha_s$ in place of α. The integrated form of Fick's equation then becomes

$$V = -\ D' \cdot \alpha_s \cdot \frac{d\beta}{dh}$$

since α_s is constant. V is the molar velocity of transfer per unit cross-section. The new value of the diffusion constant is seen to be $D'\alpha_s$, and we may now use this value for the diffusion equation for the graded system,

$$V = -\ (D'\alpha_s) \cdot \frac{d\beta}{ah} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

which reduces to the ordinary equation in a homogeneous solvent and gives zero value for the diffusion velocity when β is constant.

Since, from the equation

$$V = -\ D' \cdot \frac{d\alpha}{dh}$$

the driving force, *i.e.* gradient of osmotic pressure, is given by $RT \cdot \frac{d\alpha}{dh}$, the gradient of diffusion pressure in the graded case will be, from (3), $RT\alpha_s\frac{d\beta}{dh}$. The gradient of osmotic pressure in this case is still

$$RT\frac{d\alpha}{dh}$$

by (2)

$$= RT\frac{d(\alpha_s\beta)}{dh}$$

$$= RT \cdot \alpha_s\frac{d\beta}{dh} + RT\beta\frac{d\alpha_s}{dh}.$$

The difference between the two is therefore given by the term

$$RT\beta\frac{d\alpha_s}{dh}$$

and this may be regarded as the amount of the osmotic pressure gradient which is neutralised by the attractive forces which give rise to the difference in solubility.

Movement of a Solute in Two Mutually Diffusing Solvents.

Some experiments in this direction have been made by Thovert,[2] who filled one-half of a cylinder with a binary solution and the remaining half

[2] *Ann. Physique* (9), **2**, 405, 1914.

with the same solution to which a third component had been added.   After a suitable time the contents of the upper and lower halves were analysed. He used as solutes sodium chloride, sugar and alcohol, and experimented on all six arrangements of "additional" and diffusing solutes, using water as solvent.   He found in each case an increased concentration of the additional solute at the end of the experiment in the region towards which the diffusing component was moving.   These results are in agreement with the solubility theory in the cases where the effect of the diffusing component on the additional one is known, for alcohol decreases the solubility of salt, and salt can "salt out" alcohol, while alcohol also decreases the solubility of sugar.

In these experiments, however, the "push" effect is certainly not eliminated, and equilibrium in such a system is difficult to realise experimentally.   The condition might be fulfilled if we had a diffusion cylinder closed above and below by horizontal membranes permeable to two solvents having the same molecular volume so that the effect of each would be to cancel that of the other, and impermeable to the solute enclosed between them. The gradient would be maintained by circulation of the lighter liquid outside the upper membrane and the heavier one outside the lower one.

A qualitative experiment in such a system is easily carried out, however.   The apparatus is shown in Fig. 2 which is one quarter the natural size.   The portions of the glass tube between the constrictions *a*, *b* and *c*, were approximately equal in volume (about 3 c.c.) and the wide, short part, *d*, was about twice the capacity of either.   The bottom was drawn off into a fine capillary and the top was fitted with a tap.   During experiments the apparatus was fixed vertically in a stand which was cemented to a solid brick column, freedom from vibration thus being secured.

In common with all the diffusion experiments described in this paper, the work was done in a basement room with a double door and without windows, the temperature being controlled by an electric heater and toluene regulator, so that no part of the room varied by more than 0·2° C.

It was necessary to find pairs of organic liquids having about the same molecular volume, and showing practically no contraction on mixing.   As solute, iodine was chosen, being easy of analysis at low concentrations.   The solvents chosen were ethyl alcohol, molecular volume (58), and carbon disulphide (60) ; and carbon tetrachloride (97), and benzene (88).   The solubilities of iodine in these solvents (from Seidell's book of solubilities) and their viscosities (from Landolt and Börnstein's *Tabellen*) all at 25° C. are given in Table I.
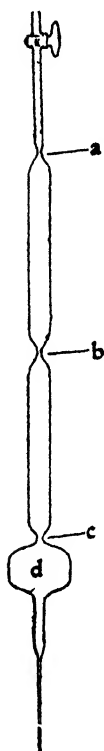

FIG. 2.

TABLE I.

Solvent.	Solubility [Iodine (gms./litre)].	Viscosity (C.G.S.).
Ethyl alcohol	180 (about)	·0108
Carbon disulphide . . .	230	·0037
Benzene	120	·0060
Carbon tetrachloride . .	30·3	·0090

Only in ethyl alcohol, and to a small extent in benzene, does the brown colour of the solution indicate solvation of the iodine. The effect of this must be to decrease the diffusion constants in the substances concerned. The diffusion constant of iodine in alcohol must therefore be less than one-third that in carbon disulphide, since the viscosity is nearly three times as great. According to Chapman's formula, therefore, the iodine will move considerably into the alcohol when the two are in contact, while on the distribution theory it will move into the carbon disulphide. The experiment is thus a test between the two theories. If both are simultaneously applicable, the viscosity effect will outweigh the solubility effect, as the ratio of the viscosities is much greater than the inverse ratio of the solubilities. In the second pair, the effects will again be in the opposite sense, both being the reverse of the former case. Here the solubility effect is very much greater than the viscosity effect, especially as the slight solvation in the benzene will decrease the diffusion constant.

TABLE II.

Solvents.	Time of Diffusion Hours.	Ratio of Concentrations (Lower Layer/Upper Layer).	
Alcohol— Carbon disulphide	0·0 6·2 8·3 10·5 23·5 Infin.	1·000 1·071 1·078 1·059 1·038 1·000	1·28
Benzene— Carbon tetrachloride	0·0 5·1 7·0 9·4 22·0 Infin.	1·000 0·849 0·805 0·851 0·922 1·000	0·25

The solutions used were made by dissolving 1 gm. of iodine in 50 c.c. of the solvent. Greater concentrations in alcohol reacted appreciably with the solvent, and this concentration is near the saturation value for carbon tetrachloride at the temperature of the experiments, namely 18° C.

The ratio of the volumes of the tube between the constrictions was measured by filling the whole with an iodine solution in carbon tetrachloride and allowing the solution to run out. A vessel containing KI solution was placed under the end of the apparatus as the meniscus passed the first constriction, a, and quickly changed for another as it passed b, the second vessel being removed as the meniscus passed c. The two portions were then titrated with decinormal thiosulphate solution. The ratio obtained was reproducible in successive experiments to one part in five hundred, and the same value was obtained using a solution in alcohol.

The diffusion experiments were conducted as follows. The apparatus was filled by suction from the top with the lighter solution as far as constriction b, and the heavier liquid was then very slowly drawn up till the liquid was nearly up to the tap. The capillary end was left dipping in a little of the heavier liquid in a small tube, to prevent evaporation of the solvent in the capillary. At the end of a certain time the tap was opened and the two portions analysed as before. Since the volume concentrations

of the two solutions were initially the same, the ratio of the concentrations of the two samples serves as a measure of the movement of the iodine. Since the two solvents diffuse into one another so that the gradient of composition continually decreases, the movement of the iodine reaches a maximum and then goes back till the concentration is again uniform.

The results are given in Table II.

The movement is seen to be in both cases as indicated by the ratio of solubilities, and to correspond approximately quantitatively with these ratios, which are given at the heads of the brackets. The movement is about three times as great in the second case as in the first, while the inverse ratio of the solubilities is also about three times as great in the second case as is the direct ratio in the first. This result indicates that the viscosity effect is included in the solubility effect. The viscosity of the two mixtures at different compositions was roughly measured, and in neither case showed either a maximum or a minimum.

The " Push " Effect of the Diffusing Component.

We have seen above that in the case where one component is flowing through the system, the gradients of activity in the static components may be expected to depend on the size of the molecules. If this is the case, we should expect an enormous " push " effect in the case of colloidal particles. An experiment was devised to test this prediction.

It was necessary to work with a system of the smallest possible dimensions, as the rate of diffusion of colloidal substances is very small. Consequently, a colloid must be chosen which can be analysed sufficiently accurately in very small quantities. Colloidal ferric hydroxide fulfils this condition, the analysis being effected by a colorimetric method, the iron being first dissolved in acid and then thiocyanate solution added.

As diffusing substance, some organic liquid having no action on the sol and soluble to a small extent in water is convenient, the gradient being maintained by keeping one surface in contact with this liquid, and allowing it to evaporate from the other. Ordinary ether was chosen, being soluble to about 12 per cent. in water and being very volatile. A 2 per cent. ferric hydroxide sol was left in contact with ether for several days, and showed no sign of coagulation or settling.

The apparatus is shown in Fig. 3 which is one-third natural size. The bulb, A, contains wet ether. It was clamped firmly in the position shown, and a test tube containing ether was placed under the limb, B, which dipped into the liquid. By sucking at C and closing the tap, the syphon tube was filled with ether. A little of the sol (concentration about 1 per cent.) was then introduced into the bottom of the test tube, and the latter raised until the end of the tube dipped into the sol. The ether was then withdrawn from the test tube by means of a pipette. On removing the test tube, a layer of sol was left in the end of B. Careful manipulation was needed, and the level of ether in the bulb had previously to be adjusted to slightly lower than the end of B. It was also found necessary previously to grease the end of B to prevent the sol from creeping round the edge : the ether of course removed most of the grease, but sufficient was left to have the desired effect. By means of filter paper and a small pipette with a bent tip, sol was withdrawn from or added to the layer till it was about 3 mm. deep. The remainder of the apparatus was then carefully placed in position, and water added to the reservoir D till the level at E was as close as possible to the end of B. The object of this

procedure was to minimise the evaporation of water from the sol layer without stopping the evaporation of ether. Ether was thus continuously diffusing downwards through the sol layer.

At the end of five days an analysis was effected as follows. The water level in E was lowered by removing water from D, and this part of the apparatus carefully removed. A fine capillary tube drawn and bent at right angles at the end was clamped so that its tip pointed upwards a little below the sol in B. By slowly turning the clamp, the tip was raised till it just touched the liquid. The liquid was drawn into the tube by capillary attraction until only a very little (about $\frac{1}{4}$ of the original quantity) remained in B. The liquid in the tube was now forced out into three test tubes, the length occupied by each sample being found by successive measurements of the distance of the meniscus from the end of the tube. The three samples were warmed with equal volumes of dilute hydrochloric acid and made up to equal volumes with thiocyanate solution, and then compared
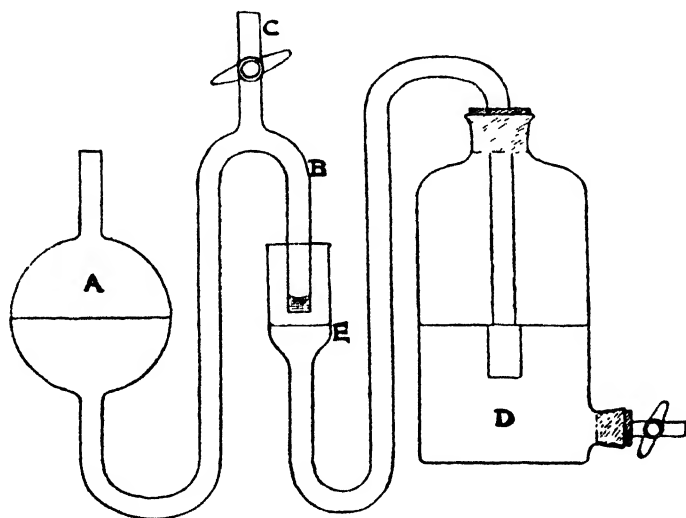

FIG. 3.

in a Dubosque colorimeter. The ratio of the volume concentrations of the ferric hydroxide in three successive fractions of the ether gradient layer was thus obtained.

The ratios for two experiments were

$$0.78 : 1.00 : 1.27$$
and $$0.76 : 1.00 : 1.19$$

the lowest layer having the greatest concentration. Since the three fractions are each about one-quarter of the original layer, the uppermost quarter being unused, and since the ether concentration will vary from 12 per cent. at the upper surface to zero at the lower one, the corresponding ether concentrations will be about

$$7.5, \ 4.5, \ 1.5 \text{ per cent.}$$

The mean mol fraction of water in the layers will therefore be

$$0.979, \ 0.988, \ 0.996.$$

Assuming that the activity of the water is proportional to its mol fraction, and that the activity of the colloid particles is proportional to their volume

concentration, it is seen that *the gradient of activity is relatively very much greater in the colloid, as was predicted by the theory.*

The agreement between the two experiments is not very good, but this is not surprising in view of the nature of the technique. The upper surface of the diffusing layer, where it is in contact with the ether is considerably curved, and this may give rise to disturbance by convection * which would have the effect of making the observed gradient in the sol too small.

Solutions of ether in water have greater viscosity than pure water, so that, on Chapman's theory, we should expect a tendency for sol to accumulate in the upper layers. The observed accumulation in the lower ones cannot, therefore, be due to the influence of the ether on the diffusion velocity.

Equilibrium of Four Substances in a Gradient of Concentration of Acetone in Water.

To determine how far the distribution theory is applicable in a ternary molecular solution where one component is diffusing through the system, it is desirable that the diffusing component should have a considerable but different influence on the solubility of the other solute, which should in any case be small, in order that we may assume the concentration and activity to be proportional over the range concerned. Both the diffusing and stationary solutes should be susceptible of exact analysis, and the system is further limited by the methods available of maintaining the gradient of the diffusing substance.

The first method tried for the latter process was to circulate the vapour of a volatile organic substance lighter than water over an aqueous layer supernatant on a layer of organic liquid such as chloroform or carbon tetrachloride, only very slightly soluble in water but capable of removing the diffusing substance. For diffusing substance, acetone was chosen, being very volatile and having a favourable partition ratio with carbon tetrachloride. Since the acetone, or whatever other diffusing substance was used, must also be lighter than the carbon tetrachloride, it was necessary by some means to stir the latter to prevent an appreciable accumulation of this substance in the upper part of the layer, which would be incompatible with maintaining a constant gradient in the aqueous layer. Attempts were made to do this by keeping part of the vessel slightly cooled, but it was found impossible to stir the carbon tetrachloride without also stirring the water and thus destroying the gradient altogether. This method was therefore abandoned, and the one described below was used. Acetone, however, was still used as the diffusing solute, as it can easily be estimated with considerable accuracy by distilling the sample into a weighed receiver immersed in a freezing mixture and measuring the quantity and density of the distillate.

Acetone has also the advantage that, although itself very mobile, it increases the viscosity of water in dilute solution, the viscosity reaching a maximum of about $1 \cdot 5$ times that of water at about 35 per cent. by weight of acetone. Since the solubility of most substances soluble in water is decreased by the addition of acetone, the viscosity effect, if it exists, will in general act in the opposite sense to the solubility effect.

The four solutes worked with, on account of their solubility being of the order required, were ammonium oxalate, lithium carbonate, potassium

* The errors due to convection in systems of this type will be discussed in a subsequent paper.

*chlorate and succinic acid. The solubility of the first three is lowered
to different extents by addition of acetone, while that of the last is increased.
The only figures available for the solubility of any of these substances in
aqueous acetone are those of Herz and Knoch*[4] *for succinic acid, but as
these were determined in solutions made up by volume, it was decided to
measure all independently.*

Excess of the recrystallised solute was sealed up in tubes with weighed
amounts of water and acetone. The tubes were kept in a thermostat and
shaken from time to time for several days. They were then broken open
and immediately on breaking each one three samples of the liquid were
quickly transferred to three weighed flasks fitted with stoppers, in order to
minimise loss of acetone by evaporation before reweighing. Analysis was
affected in the case of ammonium oxalate by adding excess sulphuric acid,
boiling off the acetone, and titrating with decinormal permanganate solution.
It was necessary to get rid of the acetone before titrating since a warm
dilute solution of acetone will itself decolorise permanganate slowly. The
lithium carbonate was titrated with decinormal HCl and the succinic acid
with $0.25N$ CO_2 – free caustic soda. The potassium chlorate samples
were carefully evaporated to dryness in weighed dishes.

It was considered most convenient, in a ternary system such as this, to
express all the compositions as mol fractions or mol ratios, putting the
molecular weight of water $= 18$ and ignoring the dissociation of the
electrolyte. The results are given in Table III.

TABLE III.—SOLUBILITY OF FOUR SUBSTANCES IN AQUEOUS ACETONE SOLUTIONS
AT $17.6°$ C.

($N_1 =$ mol. ratio, acetone/(acetone water). $N_2 =$ mol. fraction solute at saturation.)

Solute.	N_1.	N_2.	Solute.	N_1.	N_2.
Potassium chlorate	0·0000	0·00953	Lithium carbonate	0·0000	0·00331
	·0233	·00847		·0326	·00211
	·0409	·00779		·0668	·00105
	·0513	·00740			
			Ammonium oxalate	·0000	·00604
Succinic acid	·0000	·00940		·0136	·00488
	·0204	·01123		·0273	·00395
	·0337	·01267		·0344	·00352
	·0471	·01429		·0544	·00261
	·0600	·01600		·0668	·00219

The apparatus used for the gradient experiments is shown in Fig. 4,
which is two-fifths natural size. The glass bell, A, passes through the
brass cover plate, B, which has a hole turned to fit. This cover plate is
mounted on a large gas jar, C, with a ground top. The joints are all
cemented with picein. The jar is filled up to the level shown by the dotted
line, D, with an aqueous solution of the substance to be experimented on,
this being introduced through an ordinary funnel passing through E before
the long-stemmed capillary funnel, F, is placed in position. During the
experiment the acetone vapour is drawn through the tube GH, and fills the
volume of the bell above the liquid by convection, being heavier than air,
the rapid current passing only through the top of the bell so that it does
not disturb the surface of the liquid. The upper part of the liquid inside

[4] *Z. anorg. Chem*, 41, 317, 1904.

the bell is thus saturated with acetone at the pressure used, and diffuses downward through the liquid.   At the bottom of the bell, which is ground flat and is made horizontal while filling the apparatus, by suitably packing at the base of the jar till the rim is parallel to the water level, the dilute acetone solution, being lighter than the outside solution, convects upwards. If the volume of the liquid above the rim outside the bell were infinite,
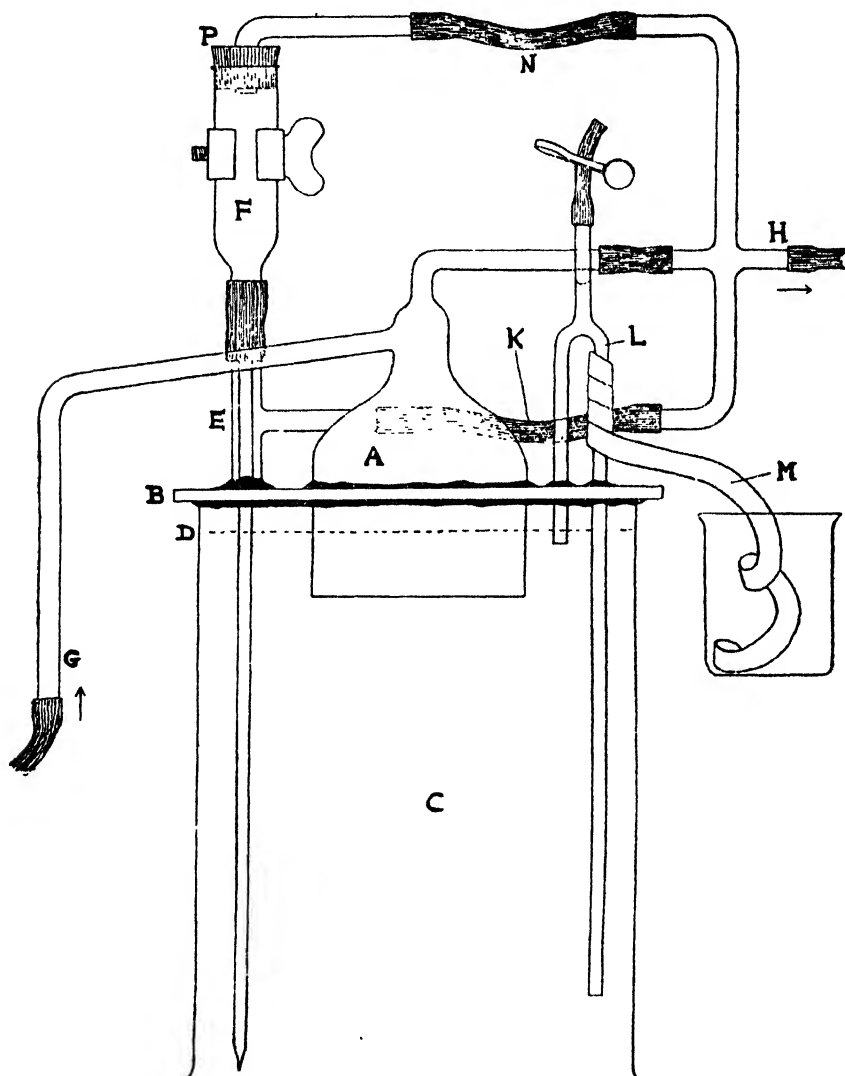

FIG. 4.

a constant gradient of acetone would be maintained in the liquid inside the bell.   In practice, however, it is convenient to maintain the water level inside and outside the same, this being insured by the connection, K. The volume above the rim outside is therefore small, but the difficulty is surmounted by means of the tube, L, one limb of which projects just below the level of the solution, and the other limb of which goes nearly to the bottom of the jar.   The tube is filled with solution by sucking, and closing

the pinchcock. The upper part of the longer limb is maintained slightly cooled throughout the experiment by means of the lamp wick, M, which is kept moist by its other end dipping in a beaker of water. Solution is thus slowly removed by convection from the upper to the lower parts of the liquid. The gradient of acetone in the bell is thus nearly constant: it constantly slightly decreases owing to the slow accumulation of acetone in the bulk of the solution. The connection K has inserted in it (not shown) a long U-tube in order to prevent convective flow of acetone vapour from H into the air space in the jar. The connection N maintains the pressure of air inside the funnel the same as that in the other parts of the system, and so makes it unnecessary to insert the stopper, P, very tightly. This is an advantage as the funnel is supported only in a retort clamp and it is necessary to remove the stopper at the end of an experiment without shaking the apparatus.

Acetone vapour was found to be most satisfactorily prepared by bubbling through a Winchester quart bottle filled with 15 per cent. acetone solution. This also prevents loss of water by evaporation in A. As acetone was constantly removed from the bottle, the latter was fitted with a funnel by which acetone could be introduced from time to time to make up to a constant level, a second bottle being inserted nearer the apparatus to damp the variations in vapour pressure. The level in the second bottle remained constant. In order to smooth out any changes in pressure, two empty Winchesters were inserted in the system, one between the bubblers and the apparatus, and the other between the latter and the pump. It was found most satisfactory to run the filter pump hard, and cut down the rate of flow by means of a piece of capillary tube inserted between the diffusion apparatus and the air reservoir on the pump side.

The depth of the diffusion layer was in each experiment about 1·6 cm. It will be seen from the second and third columns of Table IV. that the variation of concentration with height of the layer is approximately linear at the end of the experiment, an indication that equilibrium has been attained.[5]

At the end of a week or more the experiment was stopped by disconnecting the filter pump and allowing the air slowly to flow back through the capillary tube till the pressure inside the diffusion apparatus was atmospheric. The rubber lead was then removed from the end of G and the stopper from F. The funnel was then carefully filled with carbon tetrachloride which ran out slowly into the vessel C. A pinchcock was then fixed on the rubber connection K to prevent the air outside the bell from escaping. The liquid inside the bell was slowly driven upwards until it began to flow out through G. F was of course kept full of carbon tetrachlorde all the time. The first twenty drops were allowed to go to waste, since, owing to the inflow of air into the bell when the experiment was stopped, the surface layer of liquid had probably lost a little of its acetone content. A series of test tubes, which had been previously weighed along with rubber stoppers, were then used to collect successive 6 c.c. fractions of the liquid issuing from G. These were considerably longer than was necessary to hold the required amount, and not much wider in bore than the diameter of G, so that evaporation of acetone during the process was minimised. Each tube was tightly stoppered as soon as filled. Five samples accounted for about 1·5 cm. depth of the diffusion layer. About 30 c.c. was then allowed to run to waste before the sixth sample was taken.

[5] See Tanner, *Trans. Faraday Soc.*, **23**, 83-84, 1927.

In this way the part of the liquid at the bottom of the bell during the experiment was not used. In this region there is slow gravitational convection occurring, and the significance of the results would be doubtful. In the case of the ammonium oxalate experiment, the first sample was destroyed by the breaking of the distilling flask in the acetone analysis.

The apparatus was completely dismantled, cleaned, and remade between the experiments, as it was found impossible to clean it satisfactory without doing so, drying by heat being impossible on account of the picein joints. It may be mentioned here that a great advantage of the use of acetone as

TABLE IV.

Values of N_2 corresponding to the experimental values for N_1 and read off from plot of N_2 against N_1 from Table III.

$N_2' = $ mol. fraction solute in each sample.

Degree of saturation = ratio N_2'/N_2.

Sample No.	Per Cent. Acetone.	Per Cent. Solute.	N_1.	N_2.	N_2'.	Degree of Saturation.
Succinic acid, 171 hrs.						
1	11·63	5·15	0·0416	0·01360	0·00898	0·660
2	10·05	5·18	·0355	·01288	·00891	·692
3	8·60	5·20	·0301	·01227	·00887	·723
4	7·24	5·24	·0250	·01172	·00883	·753
5	5·84	5·28	·0200	·01121	·00878	·783
6	2·39	5·42	·0080	·01138	·00881	·874
Lithium carbonate, 215 hrs.						
1	10·42	0·507	0·0350	0·00204	0·00133	0·653
2	8·91	·550	·0296	·00222	·00143	·644
3	7·41	·594	·0244	·00241	·00153	·635
4	6·01	·641	·0196	·00259	·00164	·634
5	4·68	·693	·0151	·00274	·00175	·640
6	2·34	·761	·0074	·00301	·00190	·632
Potassium chlorate, 238 hrs.						
1	10·81	2·762	0·0374	0·00790	0·00452	0·572
2	9·35	2·927	·0320	·00810	·00473	·584
3	7·73	3·055	·0262	·00830	·00487	·587
4	6·23	3·166	·0209	·00854	·00499	·584
5	4·82	3·279	·0160	·00877	·00512	·584
6	3·08	3·401	·0101	·00901	·00527	·585
Ammonium oxalate, 216 hrs.						
2	9·33	1·420	0·0314	0·00366	0·00223	0·609
3	7·69	1·538	·0256	·00403	·00239	·593
4	6·07	1·643	·0199	·00442	·00253	·573
5	4·46	1·757	·0145	·00480	·00267	·556
6	2·29	1·888	·0073	·00538	·00283	·526

the diffusing component instead of, say, an alcohol, is that acetone has practically no effect on rubber, which material it would be difficult to dispense with.

Analysis for acetone was carried out as follows. A long-necked distilling flask of about 50 c.c. capacity was used, having a long side tube first bent slightly upwards to prevent carrying over of the liquid itself. This side tube was then bent down vertically and passed through a tight-fitting rubber bung into another flask of about 25 c.c. capacity immersed in a freezing mixture of ice and salt. A small vertical tube sealed into the bulb of this flask and fitted with a rubber tube and pinchcock enabled the pressure to

be equalised from time to time during the distillation. The contents of a sample were washed into the distilling flask as quickly as possible (in the case of ammonium oxalate with dilute sulphuric acid to prevent evolution of ammonia) and the stopper of the flask replaced. The volume of liquid was about 20 c.c. in all, and about 15 c.c. were distilled over. The pyknometer used had a capacity of 10 c.c. The method was previously calibrated by use of samples of acetone solutions of known content, and a graph

prepared plotting the difference in weight of the pyknometer when filled with water and when filled with distillate against the percentage by weight of acetone in the distillate. For 6 c.c. samples the method was accurate to about 0·02 per cent. acetone in the sample. During a series of analyses, the pyknometer was re-weighed with water between each pair to allow for changes in the atmospheric condition of the balance room.

Subsequent analysis of the residue in the distilling flask for the stationary solute was carried out as described above. In the case of ammonium oxalate, samples 2 and 6 were later analysed for ammonia by distilling the latter from excess of alkali into standard HCl solution. The ammonia content corresponded with the oxalate content to 1 per cent. in each case.

The results are summarised in Table IV.

The figures in the last column would be the

FIG. 5.

⊙ Succinic acid.   △ Lithium carbonate.
▽ Potassium chlorate.   ⊡ Ammonium oxalate.

activity β of the first part of this paper on the assumption that this is proportional to the mol fraction of the solute for a constant composition of the solvent mixture over the range from zero to saturation value. This assumption can only be valid for non-dissociated solutes. The corresponding assumption for completely dissociated binary electrolytes is that the activity is proportional to the square root of the degree of saturation. In all cases, however, a series of increasing figures in the last column must mean increasing activity, defined with reference to pure solute, and decreasing figures in the last column must mean decreasing activity. The figures of the last column are plotted against N_1 in Fig. 5. The dotted lines are the values that the degree
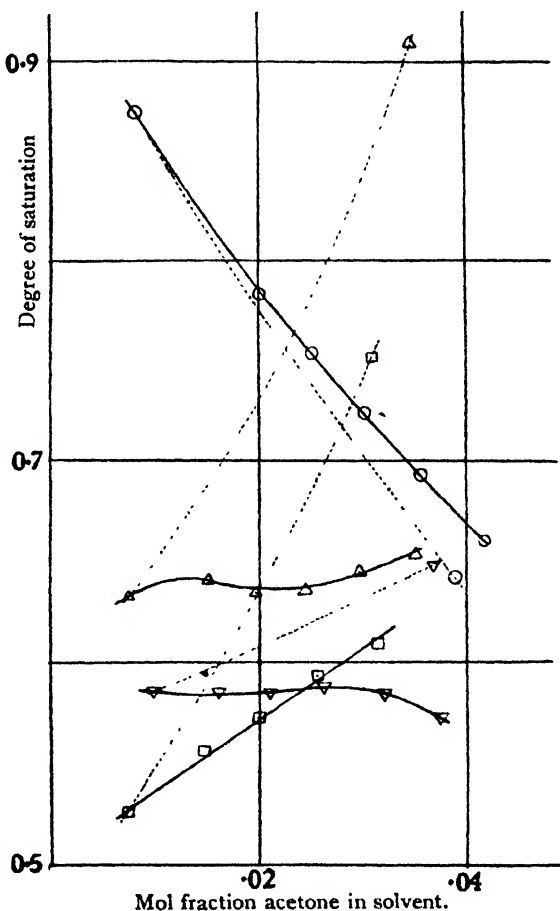
of saturation would have had if there had been no diffusion of the stationary solute relative to the water.   A comparison of the dotted and solid lines shows at once that the movement has taken place in every case towards the region of higher solubility.

Only in the case of lithium carbonate and potassium chlorate is the distribution according to solubility at all in accordance with the theory quantitatively.   In the case of ammonium oxalate, the gradient is in the same, not the opposite, sense as that of the acetone.   Since the solubility of oxalic acid is increased, like that of succinic acid, by addition of acetone, it was thought that the gradient might have affected a partial separation of alkali and acid, but the fairly close agreement between the oxalate and ammonia analyses seems to disprove this.

Succinic acid seems to be definitely anomalous in behaviour, but the anomaly admits of an explanation.   The solubility of the substance in acetone-water mixtures reaches a maximum at about 60 per cent. acetone,[4] and then decreases rapidly to a very small figure in pure acetone.   This suggests that the solubility of the succinic acid molecule *as such* decreases with increasing acetone content, but that acetone forms with it a loose compound in increasing amount as the acetone content increases.   If this is the case, part of the diffusing component is attached to the stationary one and might therefore carry it along with it, thus producing, as is actually the case, an exceptionally large opposing gradient of this latter.   Evidence in favour of the loose compound theory is afforded by the influence of succinic acid on the vapour pressure of acetone in dilute solutions (see later).   Succinic acid reduces the pressure to about ten times the extent that would be expected from Raoult's law.   The measured reduction is about 10 per cent.   This would be accounted for by this fraction of the acetone being attached to the acid.   This would mean that succinic acid exists in solution as a loose compound at a molar concentration equal to one-tenth that of the acetone.   Reference to Table III. will show that $N_2 - 0 \cdot 1 N_1$ is approximately constant for succinic acid, *i.e.*, that the increased solubility is easily accounted for by this theory.   Organic chemical considerations also render it not improbable, since acetone has basic properties under some conditions.

Were there a differential hydrolysis occurring in the case of ammonium oxalate, it is probable that the oxalic acid would behave similarly to succinic acid, and that the actual non-separation is accidental, there being a balance of two opposing effects.

It was thought that more instructive results might be obtained in a system where the activity of the stationary solute could be measured, and where there is no association with the diffusing solute.   In some electrolytes the activity at different concentrations of acetone could be determined by *E.M.F.* measurements, but it was considered preferable to use a volatile solute whose vapour pressure could be measured, this being in non-dissociating substance a measure of the activity, and to maintain the composition gradient in some other way.   The system sodium chloride—acetone was chosen, the acetone being here the stationary solute.

Measurement of the Vapour Pressure of Acetone over Dilute Aqueous Solutions containing Sodium Chloride and Succinic Acid.

The apparatus used is shown in Fig. 6 which is one-quarter natural size. The glass vessels A and B (each about 150 c.c. capacity) have ground stoppers that can be secured by stout rubber bands.   These have capillary

necks which are sealed on to the limbs of the manometer, C, which is made of 2 mm. bore tubing. The bend of the manometer is connected by rubber tubing fitted with a pinch-cock to the reservoir, D. Water is used for the manometer liquid. The stopper of vessel B is drawn out into a hook at the base from which an ampule of solution can be suspended. Vessel A is permanently in position and has a few drops of water at the bottom to keep the air inside saturated with water.

The ampules used were of 6-7 c.c. capacity, made with a thin bottom which would break easily on falling on the raised bottom of the vessel B. They were drawn off to a short neck, just wide enough to allow a hypodermic needle to enter. They were weighed before and after filling, which was affected by means of a hypodermic syringe, and the neck then drawn off to a fine capillary and bent over so as to hang on to the hook referred to above. They were filled as completely as possible compatible with this procedure. The solution with which each was filled was made from a stock solution of NaCl of the required normality, by weighing in a small bottle fitted with a well-ground stopper suitable amounts of this solution and acetone, the greatest concentration of acetone used being about 7 per cent. This mixture was kept at $17 \cdot 6°$ C. and shaken from time to time in order to saturate with air at the temperature of the experiment.

A measurement was made as follows The ampule was suspended from the hook and a known weight of the stock NaCl solution ($0 \cdot 5$ c.c.) introduced into B, previously cleaned and dried. B was then fixed in position and the whole transferred to a thermostat ($17 \cdot 6°$ C.) so that the water level came well above the stoppers. The levels of the water in the manometer and reservoir were compared and the barometric pressure noted, in order that the mean pressure inside the vessels should be known. These levels were made as nearly equal as possible, since the liquid in the ampule was saturated at atmospheric pressure. The pinchcock was then closed and manometer readings taken at intervals until there was

FIG. 6.

no further change. (Evaporation of acetone through the fine capillary neck of the ampule was so slow that it produced no appreciable change in level in twelve hours.) The apparatus was then temporarily removed from the water bath, the ampule shaken off the hook and broken, and the whole held obliquely and shaken violently up and down several times so as to wet thoroughly the sides of vessel B. It was then put back in position and
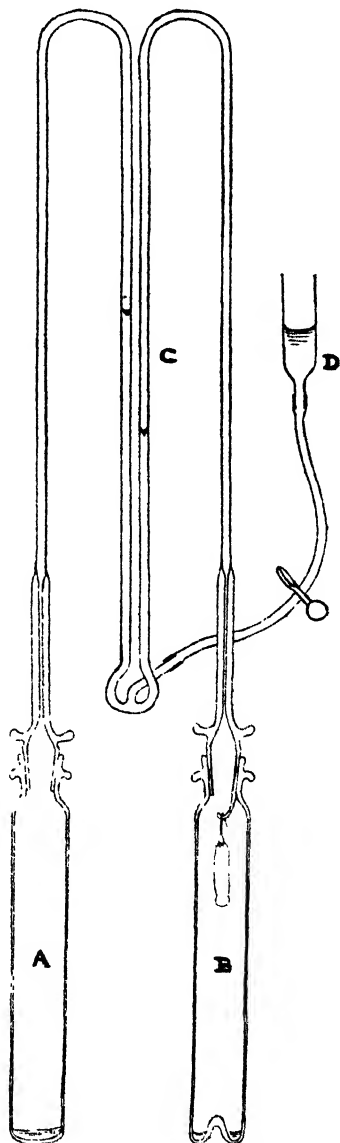
readings again taken till constant. About 90 per cent. of the saturation was thus affected quickly, and it could be assumed that the air driven into the manometer limb on the B side by the increased pressure did not contain an appreciable amount of acetone.

In order to obtain the vapour pressure of acetone from the observed readings, it was necessary to determine the total volume of each vessel up to the capillary neck and the volume per unit length of the manometer tube. Four corrections were then applied :—

(1) for the change in air pressure in the vessels owing to change in volume on alteration of the water levels (about 25 per cent.),

(2) for the non-saturation with acetone of that part of the volume on the B side above the neck of the vessel (about 5 per cent.),

(3) for the depression of the water vapour pressure on the B side due to addition of acetone (less than 1 per cent.), and

(4) for the amount of acetone evaporated in the vessel B (up to 5 per cent. of the ampule content of acetone).

Corrections (1) and (4) are exact. (2) rests on the assumption above referred to. (3) was calculated as the product of the initial water vapour pressure of the NaCl solution and the mol ratio acetone/(acetone plus water). The vapour pressure of the NaCl solutions was calculated from the figures for the lowering at 18° C. of Bousfield, given in Landolt and Börnstein's *Tabellen*. For that of the succinic acid solution, Raoult's law was assumed valid and the solute regarded as non-dissociated.

The results are given in Table V. and graphically in Fig. 7. The normality is expressed as gm. equivs. solute per 1000 gms. water.

TABLE V.—PARTIAL PRESSURE OF ACETONE OVER AQUEOUS SOLUTIONS CONTAINING SODIUM CHLORIDE AND SUCCINIC ACID, AT 17·6° C.

N_1 = mol. ratio, acetone/(acetone water).
p = partial pressure in mm. mercury.

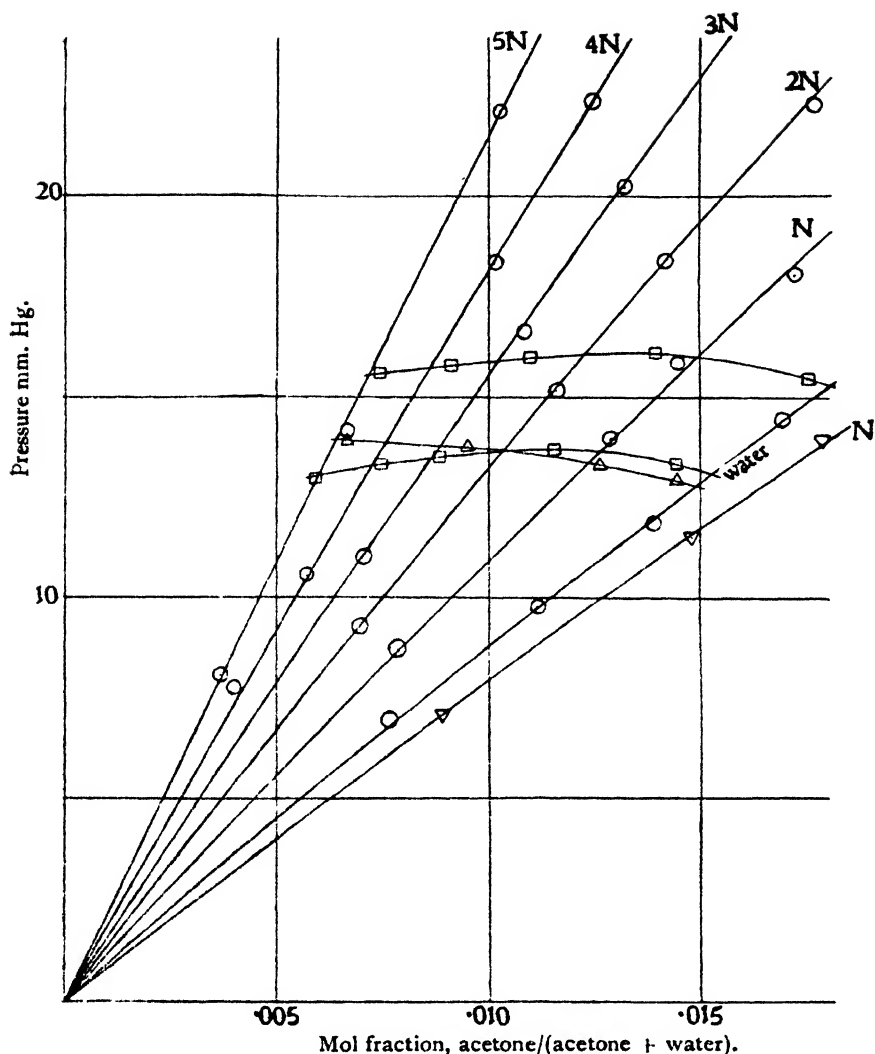|	N_1.	p.		N_1.	p.
Water	0·00770	6·94	4N NaCl	0·00400	7·76
	·01122	9·74		·00573	10·59
	·01403	11·81		·01025	18·39
	·01611	14·45		·01262	22·42
	·02115	15·37			
N NaCl	0·00688	8·70	5N NaCl	0·00369	8·06
	·01301	13·99		·00668	14·17
	·01461	15·84		·00039	22·17
	·01750	18·06			
2N NaCl	0·00700	9·29	N Succinic acid	0·00890	7·03
	·01172	15·16		·01472	11·50
	·01440	18·42		·01781	13·92
	·01798	22·32			
3N NaCl	0·00706	11·00			
	·01102	16·67			
	·01338	20·28			
	·01807	26·16			

FIG. 7.

○ NaCl solution.   ▽ $[CH_2]_2[COOH]_2$ solution.
□ Expts. 2 and 3.   △ Expt. 1.

Equilibrium of Acetone in Aqueous Solution in a Gradient of Sodium Chloride.

The apparatus finally used for these experiments is shown in Fig. 8, which is half-natural size. It consists essentially of a tall, three-legged wine-glass standing inside a gas jar. The cup of the glass, about 45 c.c. capacity and 3 cm. high is ground flat at the top. In the first experiment it was filled about half-full of powdered A.R. sodium chloride, and this was wetted with a dilute acetone solution saturated with NaCl, more being added till the level of the liquid was mid-way between that of the solid NaCl and the rim of the glass. The rest of the glass was then filled very carefully with the same acetone solution containing no NaCl, and finally the whole jar filled with this solution to a level about 1 cm. above the glass-rim. In this way an equilibrium gradient could be obtained with the

minimum amount of fall of the level of solid NaCl. During the experiment, the jar was closed with a cork through which two tubes passed as shown, these being themselves stoppered.

At the end of three days, samples were withdrawn by means of the tube A. This was a capillary tube drawn to a point at one end. It was bent twice at right angles, the other end passing through the straight part of a T-tube, B, 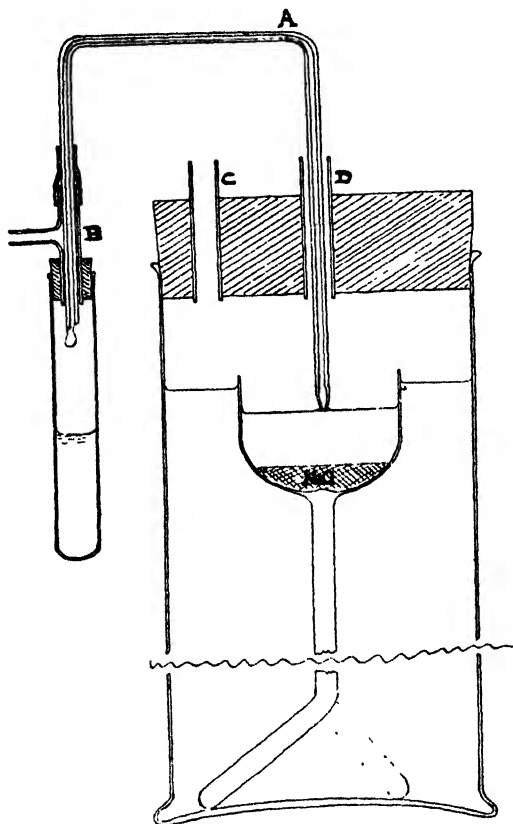and sealed to it by a short piece of rubber tube. The other end of the T passed through a rubber bung which fitted into the sampling tubes. By sucking on a rubber tube connected to the side arm of the T, solution was transferred to the sampling tube. The level of solution outside the wine glass was first lowered by means of a pipette passed through C, and the first sample then taken from the outside. The other samples were taken from inside the glass through the tube D. In taking the samples, the end of A was always kept just on the surface of the liquid.

The samples were analysed for acetone as described above, and for NaCl by evaporation to dryness in weighed dishes.

Owing to the solution of the NaCl at the bottom of the glass being fairly rapid after the first day, the experiment could not be continued for more than three days. As it was thought that equilibrium of the acetone could not be completely attained in

FIG. 8.

this time, the experiment was repeated using a saturated NaCl solution for filling the bottom half of the glass containing the same concentration of acetone as the final sample in the first experiment. The outside solution was the same as before. A third experiment was then made with a stronger acetone solution outside and a solution inside whose acetone concentration was to that of the outside solution in the same ratio as in the second experiment. The results are given in Table VI. and shown graphically in Fig. 7.

It will be seen from the graph that the acetone vapour pressure in the second and third experiments increases slightly with decreasing NaCl concentration, as would be expected from the theory, up to about $1\cdot5N$ NaCl, i.e., up to a few mm. of the top of the glass. The subsequent decrease is easily explained on the assumption that acetone is a slower diffuser than NaCl, because, as the level of solid NaCl sinks, fresh solution will descend into the top of the glass and the displacement of the excess acetone from this part will not be so near to equilibrium as the diffusion into it of NaCl.

TABLE VI.

Experiment No.	Sample No.	Per Cent. Acetone.	Per Cent. NaCl.	N_1.	Normality of NaCl.	p.
1 (75 hrs.)	1	4·47	0·69	0·01437	0·12	12·9
	2	3·75	4·82	·01259	0·90	13·3
	3	2·63	12·41	·00950	2·54	13·8
	4	1·67	21·36	·00669	4·75	13·9
2 (70 hrs.)	1	4·44	1·50	0·01440	0·27	13·3
	2	3·34	7·73	·01151	1·49	13·7
	3	2·40	13·34	·00882	2·88	13·5
	4	1·94	18·08	·00747	3·87	13·3
	5	1·46	22·41	·00590	5·03	12·9
3 (72 hrs)	1	5·37	0·93	0·01750	0·17	15·45
	2	4·00	7·11	·01390	1·37	16·1
	3	3·08	12·77	·0 095	2·59	16·0
	4	2·38	17·16	·00909	3·65	15·8
	5	1·84	21·64	·00741	4·83	15·6

Summary.

Several types of composition gradient have been studied, and in none of the results obtained is there evidence that the distribution of a solute free to move in a maintained gradient of composition is influenced by other forces than those internal ones which govern solubility and the dynamic effect of the diffusing components.

There is no evidence of a tendency to diffuse from the regions of higher to lower diffusion velocity independently of these factors, and it seems, therefore, that the statistical effect examined theoretically by Chapman must be automatically included in the solubility theory, and that therefore the factors leading to increase of diffusion velocity must also tend to decrease solubility.

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THE ELECTRO-DEPOSITION OF COBALT-NICKEL ALLOYS. PART II.

BY S. GLASSTONE AND J. C. SPEAKMAN.

The investigation of the compositions of alloys deposited from mixed buffered solutions of cobalt and nickel sulphates under various conditions, reported in a previous communication,[1] has now been extended to higher temperatures ; experiments have been carried out at approximately 50° and 90° C. No direct study of the effect of temperature in this deposition appears to have been made previously, although Foerster[2] deposited some cobalt-nickel alloys at 60°-70° C. ; he noted that at a *C.D.* of 1·5 amps./dm.²

[1] Glasstone and Speakman, *Trans. Faraday Soc.*, **26**, 565, 1930.
[2] Foerster, *Z. Elektrochem.*, **6**, 342, 1899.

the deposits contained 9·7 and 25·8 per cent. of cobalt respectively, from solutions in which this metal constituted only 2·7 and 10 per cent. of the total cobalt and nickel.   In the present work it has been found that the variation with increasing $C.D.$ of the composition of the cobalt-nickel alloys is markedly different at high and low temperatures.   At 15° the composition of the alloy remains almost independent of the $C.D.$ until the rate of removal of ions from solution by electrodeposition exceeds the rate of diffusion of these ions to the electrode; at 50° C., however, the proportion of cobalt in the deposit increases rapidly with increasing $C.D.$ before a constant composition is reached.   The behaviour under these conditions is similar to that observed in the deposition of iron-nickel alloys at ordinary temperatures.[3]   The results obtained are correlated and discussed in the light of the deposition potentials of nickel and cobalt and their alloys, and of the theory of the retardation effect of cobalt on the reversible deposition of nickel.

Experimental.

Except where otherwise stated the experimental details were the same as those described in Part I. of this series [1] for depositions at ordinary temperature.   The cells were placed in a gas-heated thermostat, the temperature of which was adjusted so that deposition occurred at approximately 50° and 90° C. in two series of experiments.   In view of the difficulty of reproducing exactly the deposited alloys a small variation in temperature is without serious effect on the composition of the deposit.   The anodes consisted of gas carbon, as in previous work, but they were not impregnated with paraffin wax.   Correction of p_H value was made with acetic acid solution containing cobalt and nickel salts in appropriate amounts.   It was noted that more frequent adjustment was necessary at elevated temperatures, especially with the solution at p_H 3·2 ; this may be attributed to the increased volatility of the acetic acid under these conditions.   The p_H values were actually measured at room temperature and so may have been slightly different from those in the deposition baths; this small difference is of no importance as the main requirement was the constancy of the p_H and not its absolute value.

The liquid in the anode compartment was of the same composition as that in the cathode section, since diffusion through the walls of the porous pot was comparatively rapid; the use of any other electrolyte would thus have affected the composition of the deposition bath.   On account of practical difficulties, $e.g.$, rapid evaporation of solutions, and frequent p_H adjustment, fewer alloys were deposited than at room temperature, but the number was sufficient to indicate quite definitely the trend of the curves drawn to illustrate the results.

Results.

The solutions examined were II., V., VI., VII., VIII. and X. at 50° C. and VI., VII., VIII. and X. at 90° C. (for compositions, see Part I. of this series [1]).   The results are represented by the smoothed curves shown in Figs. 1, 2 and 3 ; these indicate, for each solution, the variation of the composition of the deposited alloy with change of $C.D.$ The curve should be compared with those bearing the same Roman numerals in Part I.

The mean current efficiencies for alloy deposition from solution VII. (30 per cent. cobalt, and p_H 4·0) are given in Table I. ; the results for other solutions are similar.   In general, it may be seen that the current efficiency increases with rising temperature; this can be accounted for by the fact that the deposition potentials decrease more rapidly with increasing temperature

[3] Glasstone and Symes, *Trans. Faraday Soc.*, **23**, 213, 1927 ; **24**, 370, 1928.

than does the hydrogen overvoltage.   The evolution of hydrogen gas is thus retarded in comparison with the deposition of alloy as the temperature is raised.

TABLE I.

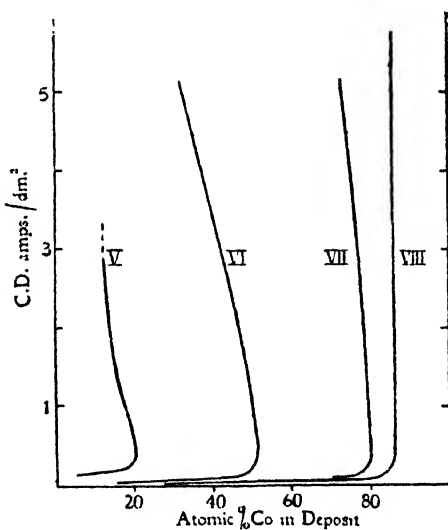| C.D. amps./dm.²	Per Cent. Current Efficiency for Alloy Deposition.		
	15° C.	50° C.	90° C.
0·2	20	40	60
0·5	42	60	65
1·0	56	71	70
2·0	64	80	81
5·0	64	85	—
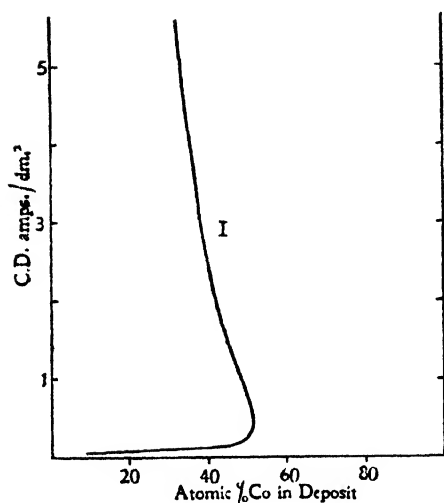
FIG. 1.

FIG. 2.

Discussion. — An examination of the curves in Figs. 1, 2 and 3 shows that they differ in an important respect from those, given in Part I.,[1] for alloys deposited at ordinary temperatures. At elevated temperatures there is, at low *C.D.*'s, a rapid increase in the cobalt content of the alloy until a maximum value is reached, although at 15° deposition at the lowest *C.D.*'s, obtainable did not indicate any such effect.   A study of the deposition potentials of nickel, cobalt and their alloys at various temperatures, quoted in Table II. from the work of

FIG. 3.

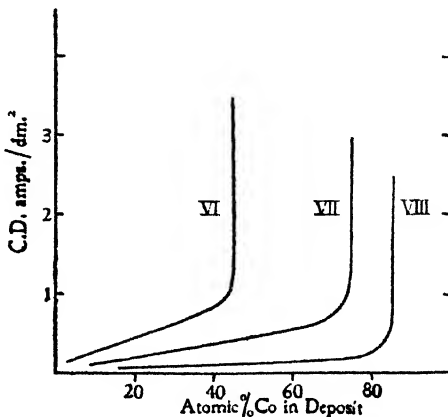Glasstone,[4] throws some light on this marked difference in behaviour.

[4] Glasstone, *J. Chem. Soc.*, 2897, 1926.

TABLE II.

Co/(Co + Ni) Per Cent. in Solution.	Deposition Potentials.		
	15° C.	55° C.	95° C.
0	− 0·57	− 0·43	− 0·29
25	− 0·57	− 0·44	− 0·32
50	− 0·57	− 0·44	− 0·32
75	− 0·57	− 0·45	− 0·34
100	− 0·56	− 0·46	− 0·36

At 15° the deposition potentials of cobalt and nickel are almost equal, so that an initial deposit containing the same proportion of these metals as in the solution, or even one containing a slight excess of cobalt, might have been expected. On increasing the $C.D.$ there should be no increasing preference for one metal to deposit more than another; the composition of the alloys deposited at ordinary temperatures are thus almost independent of the $C.D.$[1] The presence of a larger proportion of cobalt in the deposit than in the electrolyte was attributed to the retarding effect of this metal on the reversible deposition of nickel. At 55° C., however, and more so at 95° C., nickel has the less negative deposition potential, and consequently the proportion of this constituent in the alloy might be expected to increase as the temperature is raised. That this is actually the case is shown by the results in Table III., giving the compositions of the deposits with minimum cobalt content obtained at low $C.D.$'s from various solutions at 15°, 50° and 90° C.

TABLE III.

Co/(Co + Ni) Per Cent. in Solution.	Per Cent. of Cobalt in the Minimum Cobalt Deposit.		
	15° C.	50° C.	90° C.
2	26	10	—
10	56	11	2
30	80	—	10
50	90	27	14

It will be observed that for solutions containing more than 10 per cent. of cobalt at 50° C., and for all the solutions examined at 90° C., the initial deposit actually contains relatively more nickel than does the solution; this result is in harmony with the conclusions drawn from an examination of the deposition potentials.

As the $C.D.$ is raised the proportion of cobalt in the deposit increases rapidly in every case towards a maximum value; a comparison of the curves for solutions II., VI. and X. at 50° C., and of those for VI. and X. at 90° C., indicates that as far as has been investigated the composition of the alloy containing a maximum amount of cobalt is independent of the p_H of the electrolyte from which it is deposited. This conclusion is in agreement with the results obtained in the deposition of cobalt-nickel alloys at ordinary temperatures,[1] and of iron-nickel alloys at all temperatures between 15° and 90° C.;[3] it corresponds with the fact that the deposition potentials of the

iron group metals and their alloys do not depend on the hydrogen ion concentration of the electrolyte.[4,5]

The maximum cobalt content of the alloy obtained from any given solution, containing a definite ratio of cobalt to nickel, decreases somewhat with increasing temperature; the results given in Table IV. illustrate this point (see also Fig. 4).

TABLE IV.

Co/(Co + Ni) Per Cent. in Solution.	Maximum Per Cent. Cobalt in the Deposits.		
	15° C.	50° C.	90° C.
2	28	20	—
10	57	51	45
30	83	79	75
50	92	86	85

The decrease is readily accounted for by the fact that the deposition potential for cobalt becomes relatively more negative than that of nickel as the temperature is raised (Table II.).

If the *C.D.* is increased the tendency for the amount of cobalt in the deposit to diminish after the maximum is attained is less marked at the higher temperatures. This fact is brought out clearly in Fig. 4 which gives the *C.D.* composition curves for alloys deposited from solution X. (10 per cent. cobalt; p_H 5·2) at temperatures of 15°, 50° and 90° C. It appears, therefore, that in spite of the increase in current efficiency, as the temperature is raised the rate of diffusion of the ions is enhanced
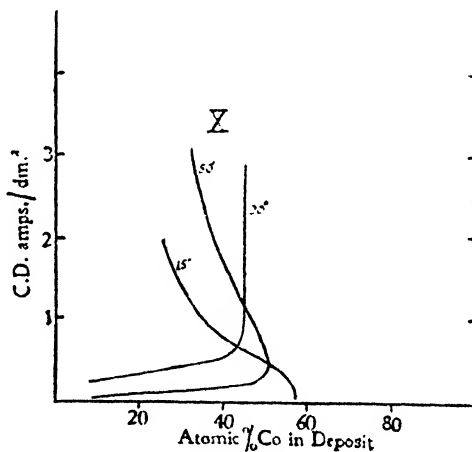

FIG. 4.

to such an extent as to cause a smaller depletion of the cobalt content of the electrolyte in the vicinity of the cathode. Incidentally the curves in Fig. 4 may be used to illustrate the danger of drawing general conclusions from a limited number of observations on the deposition of alloys. The deposits obtained from the well-buffered solution X., using a *C.D.* of 0·25 amp./dm.², at 15°, 50° and 90° C. contain respectively 56, 49 and 10 per cent. of cobalt. It would be concluded, therefore, that the proportion of cobalt in the deposit tends to decrease as the temperature is raised. On the other hand with a *C.D.* of 1·5 amps./dm.² the deposits contain 29, 42 and 45 per cent. of cobalt respectively; similar results are obtained at higher *C.D.*'s, and the conclusions drawn under these conditions would be that increase of temperature favours the deposition of cobalt. If solution X. had been diluted, or stirred, the *apparent* effect of temperature on the relative tendencies of nickel and cobalt to be deposited would be different. It is quite clear, therefore, that

⁵ Glasstone, *ibid.*, 2887, 1926.

3

conflicting results may easily be obtained by different workers, and it is only from a complete investigation, over a range of *C.D.*'s, temperatures, p_H values and total concentration of electrolyte, that general conclusions can be drawn.

There still remains to be discussed the rapid increase in the proportion of cobalt in the deposited alloys as the *C.D.* is increased from the very low values at which deposition commences. In the first place, as the *C.D.* is raised the cathode potential must become more negative, and hence the deposition of cobalt in preference to nickel will be favoured. Secondly, the increase in the cobalt content of the alloy will favour the retarding effect of this metal on the reversible deposition of nickel, evidence for which was obtained from the experiments reported in Part I. of this series.[1] The combination of these factors will result in the deposition of alloys containing markedly increasing amounts of cobalt as the *C.D.* is raised. This increase is evidently checked by (*a*) the depolarisation of nickel ion discharge resulting from the deposition of the metal in the form of a dilute alloy, and (*b*) the impoverishment of the catholyte in cobalt ions ; a point of balance will, therefore, be reached at which the proportion of cobalt in the alloy is a maximum, and is independent, over a certain range, of the *C.D.* applied. At 90° not only is the difference between the deposition potentials of cobalt and nickel greater than at 50°, but the retarding effect of the latter is probably less marked ;* hence the increase in the cobalt content of the alloy with increasing *C.D.* will be less marked at 90° C. than at 50° C. (compare Figs. 2 and 3).

It is interesting to note that the *C.D.* composition curves for nickel-cobalt alloys at 50° and 90° C. are very similar to those obtained by Glasstone and Symes[3] for nickel-iron alloys at 15° C. and 53° C. respectively. Cobalt at 90° C. and 50° C. respectively, is evidently influencing the deposition of nickel in a manner analogous to the effect of iron on the deposition at 53° C. and 15° C. This influence is probably the result of a combination of two factors, *viz.* (*a*) the difference in the deposition potentials of the metal and nickel, and (*b*) the retarding effects, which are probably related to the deposition overvoltages. The values for the deposition potential differences and the overvoltages for temperatures of 15°, 50° and 90° C., interpolated from the results of Glasstone,[4,5] are given in Tables V. and VI.

TABLE V.—DEPOSITION POTENTIAL DIFFERENCES.

	15° C.	50° C.	90° C.
Iron and Nickel . .	0·11	0·07	0·15
Cobalt and Nickel . .	−0·01	0·03	0·06

TABLE VI.—DEPOSITION OVERVOLTAGES.

	15° C.	50° C.	90° C.
Iron	0·22	0·04	Nil
Cobalt	0·25	0·16	0·06

At 90° C. the difference in the deposition potentials of cobalt and nickel is 0·06 volt, whereas the difference for iron and nickel at 50° C. is 0·07 volt ; hence the effect of this factor will be the same in both cases. It may be argued, therefore, that the retarding effect of cobalt on the reversible deposition of nickel at 90° C. is the same as that for iron at about 50° C.

* Compare the similar effect of iron at elevated temperatures.[3]

The overvoltage for the deposition of cobalt at 90° C. is 0·06, and that for iron at 50° C. is 0·04 volt; the similarity of these results suggests that the retarding effect of a given metal on the deposition of nickel is connected in some manner with the irreversibility of the former. At 50° C. the difference between the deposition potentials of cobalt and nickel is 0·02 volt, but the difference for iron and nickel at 15° C. is 0·11 volt; this discrepancy in favour of nickel deposition in the latter case must be balanced by a greater retarding effect of iron at 15° C. than of cobalt at 50° C. ; in harmony with the views expressed it is found that the irreversibility for the deposition of iron at 15° C. is 0·22 volt, whereas that for cobalt at 50° C. is 0·16 volt (Table VI.). A further study of the deposition of alloys of iron and nickel, and of cobalt and nickel at temperatures below 0° and above 100°, although difficult, would probably be of considerable theoretical interest.

Summary.

(1) The investigations already made of the compositions of the alloys of cobalt and nickel deposited from well-buffered solutions of definite hydrogen ion concentration containing various mixtures of the sulphates of these metals, at a series of current densities, have been extended to higher temperatures

(2) The relative tendency for cobalt and nickel to deposit was found, as expected from previous results, to be independent of the hydrogen ion concentration of the electrolyte.

(3) The alloys deposited at very low current densities contain decreasing proportions of cobalt as the temperature is raised ; this proportion is, in general, less than that in the solution for depositions made at 90° C.

(4) With increasing current density the fraction of cobalt in the deposited alloy increases rapidly until a constant maximum cobalt content, independent of current density, is attained ; this maximum decreases with increasing temperature.

(5) The influence of cobalt on the deposition of nickel at 50° C and 90° C. is very similar to that of iron at 15° C and 50° C. respectively.

(6) The theoretical basis of the results is discussed in terms of the deposition potentials and overvoltages of the metals concerned.

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FORMATION OF METHANE DURING THE ELECTROLYSIS OF POTASSIUM ACETATE, AND THE MECHANISM OF KOLBE'S ELECTROSYNTHESIS.

By S. N. Shukla and O. J. Walker.

Most of the controversy concerning the mechanism of Kolbe's electrosynthesis has centred round the respective merits of the so-called "discharged ion" and "oxidation" theories to account for the undoubtedly complex phenomena which occur at the anode.[1] In recent years, much

[1] Gibson, *J. Chem. Soc.*, **127**, 475, 1925; Fairweather and Walker, *J. Chem. Soc.*, 3111, 1926; Fichter, *J. Soc. Chem. Ind.*, 347, 1929.

valuable work has been done by Fichter and his co-workers, particularly with the object of showing that peroxides are formed as intermediate products at the anode. The intermediate formation of acetyl peroxide during the electrolysis of potassium acetate can be interpreted in terms of both of the above theories, and the proof of the formation of peroxides will not afford a certain criterion to distinguish between the two views. Although the peroxide theory has been accepted by Fichter, it has been criticised, amongst others, by Müller[2] and by Walker,[3] who showed that one of the strongest arguments against it, in the case of the electrolysis of acetates, was the absence of methane in the anode gases, in spite of its presence amongst the decomposition products of acetyl peroxide, often in large amounts. When this criticism was made, no evidence had been obtained for the formation of methane in the direct current electrolysis of aqueous potassium acetate solutions, although Baur[4] obtained methane from acetate solutions using commutated current, and Petersen[5] from the electrolysis of fused acetates. Evidence has now been obtained that methane is actually formed at the anode during the electrolysis of aqueous acetate solutions under certain conditions. The possibility of methane being present in the anode gases was indicated, in the first place, by the fact that during the course of a large number of analyses, in which the anode gases were analysed separately from the hydrogen, the explosion analysis of the combustible constituent gave results, which in many cases did not agree with the assumtion that it was purely ethane. The values of C/A, where C is the contraction on explosion and A the amount of absorption by potash, lay in general between $1 \cdot 25$ and $2 \cdot 0$, which are the theoretical values for pure ethane and methane respectively.

It seems surprising, in view of the large number of investigations on Kolbe's reaction, that the presence of methane should have been overlooked. It should be remembered, however, that previous analyses of the gaseous products of electrolysis have been confined almost entirely to the mixed anode and cathode gases, i.e. to a mixture containing a large proportion of hydrogen. If it is assumed that only ethane and hydrogen are present in the combustible residue after removal of the other constituents (and this has usually been done either directly or implicitly), then the presence of any methane, particularly in relatively small amounts, may easily remain undetected, since $2CH_4$ is equivalent to $C_2H_6 + H_2$, i.e. the CH_4 simply acts as a mixture of C_2H_6 and H_2. Moreover, previous analyses have usually been made with gases obtained by electrolysing at comparatively high $C.D.$ and as will be shown later, the amount of methane formed is appreciable only at low $C.D.$'s.

In order to make certain, however, that the combustible gas does contain methane as well as ethane, it was decided to remove the ethane from the mixture by cooling it with liquid air, and to burn the uncondensed methane separately. This was done by transferring the combustible residue, after the removal of carbon dioxide and oxygen, from the Bone and Wheeler apparatus to an evacuated tube cooled in liquid air. After standing for some time, any uncondensed gas was pumped off by means of a Töpler pump. The presence of methane would be proved if this uncondensed residue were found to be a combustible gas giving a ratio of $C/A = 2 \cdot 0$ on explosion.

In a large number of analyses this was found to be the case. The following values, for example, of C/A were obtained from the explosion of

[2] Muller, *Z. Electrochem.*, **28**, 103, 1922.   [3] Walker, *J. Chem. Soc.*, 2040, 1928.
[4] Baur, *Z. Electrochem.*, **29**, 105, 1923.   [5] Petersen, *Z. Electrochem.*, **20**, 328, 1915.

the residue of the gas evolved at the anode in the electrolysis of potassium acetate solutions, after removal of CO_2, O_2, and of ethane as described above: 1·96, 2·01, 1·93, 1·99, 1·99, 1·92, 1·93, 1·89, 2·00, 2·10 (average = 1·97). Explosion of the condensed gas separately gave $C/A = 1·25$. These results show conclusively that methane is present in these cases in the anode gases from the electrolysis of potassium acetate.

The preliminary experiments indicated that the current density was an important factor, methane being found in general only in the anode gases obtained by electrolysis with low current density. In order to investigate more closely the conditions under which methane is formed, solutions of potassium acetate (containing an equivalent amount of free acetic acid) of different concentrations were electrolysed at various current densities at the ordinary temperature. A platinum wire anode, length 4·4 cm. and diameter 0·1 cm., was used and the anode gases were collected separately. The analyses were carried out in a Bone and Wheeler apparatus over mercury. After removal of carbon dioxide and oxygen, the combustible residue was transferred to the liquid air cooling apparatus mentioned in the preceding paragraph, and the uncondensed portion pumped off and measured. Preliminary measurements with known mixtures of pure methane and ethane showed that the contraction after cooling with liquid air was a sufficiently accurate measure of the amount of ethane present in the mixture. In many cases the condensed ethane was also pumped off, collected separately and exploded. In the analysis of the anode gases, the residual gas not condensed by liquid air was not assumed to be entirely methane, since the presence of more or less accidental amounts of nitrogen had to be allowed for, due to air dissolved in the original electrolyte or admitted during the course of the analysis. The uncondensed gas was therefore exploded and the methane determined from the explosion results, the value of C/A acting as a check on the analysis.

The results are given in Table I.

It will be seen, firstly, that the quantity of methane is appreciable only when the electrolysing current has a value below about 15 m.a., corresponding with a current density of about 10 m.a./sq. cm. The results with the N solutions show this particularly well. In a few cases, small amounts of methane were obtained with comparatively high current densities. Secondly, the proportion of methane to ethane for a given current density is greater the more concentrated the solution. In the most favourable case, using a 3·5 N solution, almost twice as much methane as ethane is formed. Thirdly, methane is formed apparently only along with ethane. From the results with 0·5 N and 1·0 N solutions, it is evident that no methane is evolved as long as oxygen is the main gaseous product. These results may be summed up by saying that methane is formed within a definite limit of current density.

The formation of methane under certain conditions at the anode has thus been established, but it is difficult to see in what way the methane can have been formed. One must admit that in these cases the argument that the products of the electrolytic reaction are not the same as those of the thermal decomposition of acetyl peroxide, does not hold, and the peroxide theory provides, therefore, a possible partial explanation. It must be emphasised, however, that at ordinary current densities, such as are used in the electrolytic preparation of ethane, no appreciable amount of methane is produced, and one must suppose that under these conditions the acetyl peroxide decomposes in a different manner. If the methane is

produced by thermal decomposition of ethane [6] due to a region of higher temperature at the anode surface, then one would expect the proportion of methane to ethane to increase with the current density, since the temperature effect at the anode surface would then be greater. As seen from the last column in Table I., however, the ratio CH_4/C_2H_6 decreases with increasing *C.D.* In this connection, it is interesting to note that in many reactions in which a disruption of the acetic acid molecule or of the acetate radicle takes place, methane occurs amongst the reaction products,

TABLE I.

Concentration of Electrolyte.	Current Milliamps.	Per Cent. CO_2.	Per Cent. O_2.	Per Cent. CH_4.	Per Cent. C_2H_6.	Per Cent. Residue.	$\dfrac{CH_4}{C_2H_6}$.
$0·5N$ CH_3COOK (+ $0·5N$ CH_3COOH)	1	4·2	83·3	0	3·3	9·2	0
	2	4·9	87·7	0	1·7	5·7	0
	3	6·3	87·3	0	1·0	5·4	0
	4	7·4	87·0	0	0·5	5·1	0
	5	9·9	82·3	0	1·3	6·5	0
	6	38·4	15·3	9·0	34·2	3·1	·26
	7	50·4	4·4	7·7	35·9	1·6	·22
$0·5N$ CH_3COOK (+ $0·5N$ CH_3COOH)	5	34·8	5·6	14·5	35·8	9·3	·41
	10	32·8	1·8	11·1	47·9	6·4	·23
	15	41·6	2·9	6·6	44·4	4·5	·15
	25	43·2	1·8	3·2	48·2	3·6	·07
	50	46·9	1·4	0·6	46·2	4·9	·013
	100	47·9	1·8	0	46·5	3·8	0
$1·0N$ CH_3COOK (+ $1·0N$ CH_3COOH)	1	11·5	76·5	0	2·3	9·8	0
	2	13·9	76·7	0	1·6	7·8	0
	3	40·6	14·0	17·7	23·6	4·1	·75
	4·3	56·4	1·7	8·8	31·3	1·8	·28
	5	56·6	1·1	7·7	32·9	1·7	·23
	6	57·3	0·9	6·3	34·4	1·1	·18
	10	56·9	0·5	3·7	37·5	1·4	·10
	15	55·4	1·0	2·1	40·2	1·3	·05
	25	53·6	0·8	1·6	42·3	1·7	·04
	35	55·9	0·7	1·2	40·6	1·6	·03
	50	56·6	0·9	1·0	39·7	1·8	·025
	100	58·5	0·6	0·5	39·5	0·9	·012
	300	54·8	0·8	0·6	42·2	1·6	·014
$3·5N$ CH_3COOK (+ $3·5N$ CH_3COOH)	1·5 – 2·0	67·3	0·4	19·8	10·5	2·0	1·89
	4·0 – 6·0	66·0	0·4	15·3	16·3	2·0	·94
	8	59·5	1·0	5·1	32·1	2·3	·16
	10	55·4	0·6	0	36·9	7·1	0
	15	50·5	1·0	0	42·8	5·7	0
	25	48·9	1·8	0	44·7	4·6	0
	200	59·4	0·3	0	46·3	0	0

e.g. fusion of acetate with soda-lime, action of persulphate on acetate, action of barium peroxide on acetic anhydride, decomposition of acetyl peroxide, photolysis of acetates.

It has already been pointed out that the intermediate formation of acetyl peroxide may be admitted according to both the discharged ion and oxidation theories. Since a certain amount of misunderstanding appears to have arisen in the recent literature, regarding the interpretation of the evidence for and against these theories, this opportunity is taken to discuss

[6] Fichter, *Helv. Chim. Act.*, **13**, 98, 1930.

the subject further. Wieland and Fischer [7] state that it is of no importance which view we adopt, since the end result is the same. Fichter [8] says the same thing : " We fail to see the difference between the chemical oxidation of an acid and the discharge of its anions at the anode. Both reactions are identical and consist in a loss of one negative charge per equivalent." Further,[9] in comparing Kolbe's reaction with the action of fluorine on acetates, he says : " The anodic reaction can be formulated as a simple oxidation ; the reaction with fluorine on the other hand as a reaction between ions. It is solely a question of convenience, and one which does not suppose any change in the mechanism of the reaction." Yet in spite of this, he states elsewhere [10] : " The purely chemical imitation of the Kolbe electrosynthesis of hydrocarbons by means of gaseous fluorine, proves conclusively that synthesis is due to oxidation." Now admittedly the *net* result of the two theories is the same, and this obviously must be the case since they are both put forward to explain the same set of facts. But it is quite incorrect to assume that the mechanism of the reaction must be the same. In fact, it simply ignores one of the most important questions at issue, *viz.*, whether oxygen is necessarily formed as an intermediate stage at the anode.

It is by no means clear whether those who uphold the oxidation theory consider that the oxygen is produced from discharge of the CH_3COO' ion and reaction with water

$$2CH_3COO + H_2O = 2CH_3COOH + O \qquad . \qquad . \quad (1)$$

or by discharge of oxygen or hydroxyl ions. The latter mechanism is highly improbable, when one considers the ease with which ethane formation occurs in non-aqueous solvents and, also, the change to the Hofer and Moest reaction when the electrolyte is made alkaline. Work at present in progress shows that the abnormally high value of $2\cdot54$ volts for the so-called discharge potential of the acetate ion [11] is not correct, or that, at any rate, ethane is evolved below this potential. If one supposes that the oxygen is produced by the action of discharged acetate radicles on water, then the difficulty of explaining the reaction in non-aqueous solvents still arises. Moreover, it is not clear whether it is to be supposed that the acetic acid which is oxidised according to the equation

$$2CH_3COOH + O = C_2H_6 + 2CO_2 + H_2O \qquad . \qquad . \quad (2)$$
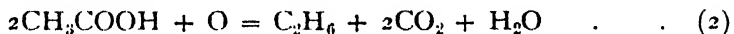
is simply the acid in the solution immediately in contact with the anode, or whether it is what one might call "nascent" acetic acid produced by reaction 1. There is no reason to suppose that the freshly-formed acetic acid at the anode has properties differing from those of the acetic acid in the solution which is not oxidised to ethane and carbon dioxide.[12] The electrolysis of concentrated acetic acid solutions, containing small quantities of sulphuric acid, shows clearly that the ethane reaction does not take place when oxygen evolution is increased.[13]

It remains now to dispose of certain criticisms which have been made of the discharged ion theory, since they have been repeated several times ;

[7] Wieland and Fischer, *Ann.*, **446**, 60, 1925.
[8] Fichter, *J. Amer. Electrochem. Soc.*, 274, 1929.
[9] Fichter, *J. Chim. Physique*, **23**, 494, 1926.
[10] Fichter, *Helv. Chim. Act.*, **9**, 697, 1926.
[11] Preuner and Ludlam, *Z. physikal. Chem.*, **59**, 682, 1907.
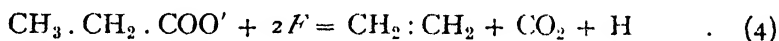[12] Fairweather and Walker, *loc. cit.*, 3119.
[13] See also Schall and Thieme-Wiedtmarckter, *Z. Elektrochem.*, **35**, 343, 1929.

quite recently again by Fichter.[1] It is maintained that, if this theory is correct, we should expect Kolbe's reaction to take place the more readily the greater the dissociation of the salt used, whereas experiments show that salts of the strong sulpho-aliphatic acids do not give a Kolbe synthesis. Moreover, a solution of a benzoate which contains benzoate ions does not give diphenyl on being electrolysed. It must be remembered that the concentration of the discharged ions at the anode is the predominant factor, and only to a lesser extent is the result due to the concentration of the undischarged ions in the solution, in so far as they affect the composition of the electrolyte. Further, the failure to find any representative of the aromatic series of acids which would undergo a Kolbe reaction in an aqueous solution of its salts, does not mean that the anions of such acids are not discharged at the anode, as is implied by Fichter. It is obvious that the discharge of an anion is not necessarily followed by reaction to give the Kolbe synthesis. The discharged anions can react in several ways, *e.g.* with one another, with the solvent or with substances in solution; the particular way in which they will react will depend on a large number of factors, *e.g.* their concentration at the anode, their chemical nature, the concentration of the solution, temperature, nature of anode, etc. The fact that the Kolbe synthesis is far from being general is not surprising, and constitutes no argument against the discharged ion theory.

Another argument given several times by Fichter[1] against the discharged ion theory is that "one molecule of propionate, or one anion of propionic acid, requires sometimes one and sometimes two electric units for its discharge." This statement is quite wrong. It is obvious that one gram-ion of a monobasic acid like acetic or propionic acid always requires one Faraday for its discharge. It is stated that a propionate in yielding ethylene apparently consumes two Faradays per molecule, whereas an acetate in yielding ethane consumes only one, but this is due to the fact that the equation

$$2CH_3 . CH_2 . COO' + 2F = CH_2 : CH_2 + CO_2 + CH_3CH_2COOH \quad (3)$$
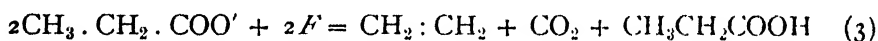
is expressed incorrectly, as follows

$$CH_3 . CH_2 . COO' + 2F = CH_2 : CH_2 + CO_2 + H \quad\quad . \quad (4)$$

"Equation" (4) naturally gives a surplus of 1 Faraday on the left-hand side because it has been obtained by subtracting CH_3CH_2COO' from the left-hand side of equation (3) and only CH_3CH_2COO from the right-hand side. This is equivalent to saying that the equation $2OH' + 2F = HOH + O$ can be written $OH' + 2F = H + O$.

Summary.

(1) It has been shown that under certain conditions methane is present along with ethane amongst the anode gases produced during the electrolysis of aqueous potassium acetate solutions

(2) The conditions favourable to the formation of methane appear to be low current density and high concentration of the electrolyte.

(3) The mechanism of Kolbe's electrosynthesis and the recent work of Fichter are discussed.

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THE HARDNESS TESTING OF ELECTRO-DEPOSITS AND OTHER THIN METALLIC COATINGS.

By Hugh O'Neill, M.Met., D.Sc.

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The determination of the "hardness" of electro-deposits and metallic coatings is of importance primarily as a means of judging the mechanical behaviour of such thin layers, and secondly as a method of studying the process, or series of processes, by which the finished coated article is produced. In general the mechanical worth of a deposit depends upon its resistance to wear ; and sometimes its brittleness may be an important criterion. The tests for these particular features, however, are not yet as well-established as those which determine the "indentation hardness" of the metal. Unfortunately, the latter property does not bear a definite relation to the abrasion properties, but it may be said that over a range of metals of different hardnesses, the order of their resistance to certain kinds of wear will generally correspond with the order of their indentation hardness.[1] The main purpose of this paper is to describe some tests on the indentation principle (including scratch tests) which it is hoped will at least serve to discriminate one commercial coating from another. The limitations for this are at present that the deposits must not be extremely hard and not much less than 0·0005 inches in thickness.

Abrasion and Wear Testing.

This difficult subject was ably reviewed by Hankins[2] in 1929. Amongst the procedures which have been utilised for the abrasion testing of coatings, one may mention the empirical tests by sandblasting and "tumbling." Piersol,[3] and Macnaughtan and Hothersall[1] have also developed methods for determining resistance to wear.

Since Hankins reported on the confused nature of the available results of wear tests, the effect of oxidation has been brought into prominence by the researches of Fink.[4] It is likely that future work, undertaken with the oxidation factor in mind, will lead to more promising results than have hitherto been obtained. Meanwhile the present practice appears to be to use imitative tests which probably give some indication of the behaviour of metals exposed to similar circumstances.

[1] Macnaughtan and Hothersall, *Metal Industry* (London), p. 321. March 21st and 28th, 1930.
[2] Hankins, *Proc. Inst. Mech. Eng.* (1) 317, 1929.
[3] Piersol, *Trans. Am. Electrochem. Soc.*, **56**, 371, 1930.
[4] Fink, *Organ Fortschritte Eisenbahnwesens*, **20**, 405, 1929.

Some Factors which Influence Testing.

Below are discussed certain factors which must be considered in the abrasion, indentation or scratch testing of thin metallic layers.

(1) **Surface Finish.**—Mechanically-plated articles like "rolled gold" will probably have a smooth surface if the finishing rolls were in good condition. Some electro-deposits have a smooth bright exterior when taken from the plating bath, but on the other hand many are rough and even nodular in surface texture. The latter condition is unsuitable for most types of hardness test, and it may therefore be necessary to grind the specimen, rub it on fine emery papers and perhaps finish with a metallographic polish before indenting. The danger about such a procedure is that the deposit may become altered to an extent which will give inaccurate results. A suitable bright annealing which would remove any surface strain-hardening due to polishing cannot be applied, as it would in all probability affect the natural hardness of the deposit itself besides allowing diffusion of the basis metal to take place. The author finds that for his scratch test described below he can in many cases secure sufficiently satisfactory results with the use of ooo emery and slight hand-polishing with selvyt dipped in "Silvo." Alternatively the hard Beilby layer may be removed by light etching.

A measure of the degree of surface roughness would probably be of utility. It should be possible to obtain such a measure in the case of plane deposits by French's " angle of optical disappearance " method as used for ground glass. Cylindrical surfaces might similarly be examined by arranging the pivot in French's test at right angles to the axis of the cylindrical specimen, or alternatively, by using a method described by A. H. Plund.[5] In this case an optical pyrometer measures the brightness of the standard light reflected from a rotating test piece.

If coatings may be classified as to roughness by these means, then the requisite surface for a given hardness test may be specified.

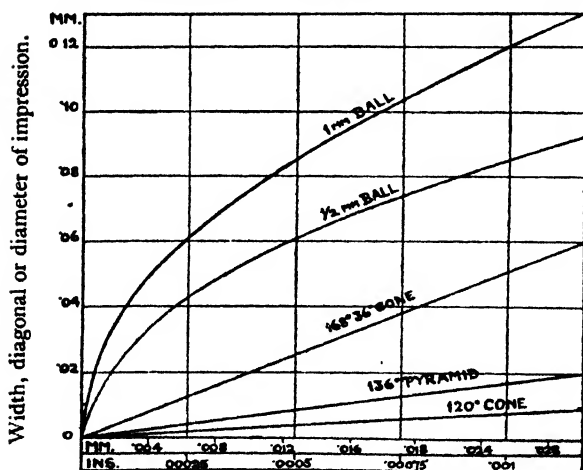(2) **Thickness of Deposit.**—For ball indentation tests Moore [6] has shown that the metal to be examined must have a thickness no less than seven times the depth of the indentation. If the supporting material is of practically the same hardness as the test deposit, then it is likely that a factor of less than seven could be tolerated. For a pointed 136° square pyramid indenter as used in the Vickers test, a recent investigation by Hankins [7] indicates that the minimum thickness of test metal is 1·5 times the diagonal of the indentation, which is equivalent

FIG. 1.—Minimum thickness of test metal.

[5] Plund, *J. Opt. Soc. Am.*, 20, 1930.
[6] Moore, *Proc. Int. Assoc. for Testing Materials*, 1909.
[7] Hankins, *Engineering*, 324, Sept. 12th, 1930.

to 10·5 times its depth.   For a pointed 120° cone tool like the Rockwell indenter, one may assume that it will require at least the same relative thickness as the pyramid.   That would be 3·04 times the diameter of the conical indentation, but to be on the safe side it is perhaps desirable to use a factor of 3·25.

In Fig. 1 is represented graphically the calculated minimum thickness of coating which may be accurately tested with various indenting tools loaded so as to produce indentations or scratches of various sizes.   The factor for a 90° cone as used in the Martens scratch test is not known, but will be higher than that for a 120° cone.   It is obvious from Fig. 1 that only those indentation tests which make a very shallow but measurable impression are of any service for testing thin commercial coatings.

(3) **Optical Difficulties in making Measurements.**—Since the minute indentations in these tests have generally to be measured under a microscope, a limitation of an optical nature arises.   With vertical illumination the minimum size of impression which is sufficiently well defined to be observed depends upon the depth of that impression.   If it is unduly shallow it reflects the incident light almost in the same way as the main background, and is consequently practically invisible.   Referring to Fig. 1, it is quite likely that for a deposit of 0·004 mm. thickness, the maximum permissible impression of 0·034 mm. width made by a ½ mm. diameter ball will be measured more easily and accurately than that of 0·048 mm. permissible width produced by the 1 mm. tool.   The author is inclined to the view that a ½ mm. ball would probably be a very satisfactory indenter for this type of work.

Te get the best contrast effects for reading shallow indentations and scratches it is desirable to stop down the microscope as much as possible ; to allow the incident light to pass through an adjustable narrow slit, and to use an objective of ¼-inch or ⅛-inch focal length.   Dark ground illuminating objectives sometimes show up a scratch which is otherwise too obscure to measure.

(4) **Internal Stress in the Coating.**—Metallic coatings, especially electro-deposits, may be internally stressed to a high degree.   The outer surface is generally in tension, and consequently if an indentation or scratch be made upon it, the liability is for the tensile forces to deform the coating and slightly open out the impression.   This is most likely to occur with sharp pointed tools.   An example of the effect is the nicking with a penknife of the outer face of a piece of rubber which is internally stressed by being bent double.   The tendency under the circumstances described is for the hardness result to be low.   The matter is raised here only as a theoretical possibility : whether it has any appreciable effect in practice remains to be seen.   The author has, however, noticed that in the scratch testing of a 0·0005 inch fairly soft dull deposit of chromium, cracks appeared at the base of a scratch when the higher loads were used.   These may be due to internal stress in the deposit.

(5) **Undue Softness of the Basis Metal.**—With the indentation type of test difficulty may arise if the basis metal is very soft compared with the coating which it supports, or unless the latter is sufficiently thick to carry all the effects of the testing deformation.   In this case, instead of a normal indentation being produced, the coating partly sinks into the backing metal.

If it is imperative to attempt an indentation or scratch test under these conditions a trial may be made to strip the coating from the basis metal. Should good adhesion prevent this, then it may be possible to employ a

solvent to remove the backing metal and leave the film of coating intact. This resulting thin metallic foil would afterwards require to be mounted by adhesion * to some flat hard material.   The author has made experiments with Canada balsam for mounting 0·001 inch thick copper foil on to glass. The advantage of a glass slide for this purpose is that one can observe whether the indentation is marking the underside of the foil, and in the trials which were made, this generally was the case.   An iron film 0·004 inch thick has however been mounted and successfully scratch tested as reported in Table V.   Further work is required in this direction before a satisfactory technique can be described.

(6) **Local Variations in Electro-Deposits.**—The physico-chemical conditions may vary at different localities of a metal plate which is undergoing electro-deposition, and this may give local variations in the properties of the deposit.   If hardness tests are being made on a series of plates it is desirable to select the same locality in each.   The author generally chooses the centre of the face of the specimen.

Indentation Testing.

The Brinell ball indentation test has been standardised by the B.E.S.A. for general purposes, and is now very widely used for the examination of metals.   Macnaughtan [8] successfully employed the 1 mm. diameter steel ball with an applied testing load of 10 kg. to investigate the hardness of electro-deposits having a minimum thickness of several hundredths of an inch.   Commercial deposits are generally much thinner than this, however, and as an extreme case chromium coatings may be only thirty millionths thick.   General work with silver, nickel, etc., is more frequently concerned with layers of about 0·0005 inch, and consequently it is desirable to be able to test such deposits.

For the purposes of studying the directional hardness of metallic single crystals, the author has constructed a scratch machine [9] which has also been used for conducting scratch tests on metals at different temperatures.[10]   At the suggestion of Professor C. H. Desch, the instrument has been tried, as described in this paper, on thin metallic coatings, in order to determine its possibilities as a test for them.   The machine has proved to be robust and reliable in operation, and uses as an indenting tool a polished hemispherical diamond of exactly 1 mm. diameter of curvature as tested by optical projection.   Such an indenter avoids the criticisms which have always been levelled against sharp-pointed scratching tools in that they are liable to chip or splinter during use, and that they are difficult to maintain at some specified simple contour.   Because of certain low-temperature work the author's machine has hitherto always been used with steam circulating round the bearing of the indenter spindle in order to maintain a constant viscosity of the castor oil lubricant.   For purposes of uniformity the same conditions have been maintained in *all* this present work, and consequently *it must be remembered in considering these results that the diamond is sensibly hot during the test.*   There is no reason, however, why a cold bearing should not be used.

Reference to the papers quoted above must be made for details of construction and procedure, but the complete instrument combines many

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* Adhesive dental waxes such as Ash's Model Cement (M.P. 56° C.) or Caulk's Sticky Wax (M.P. 66° C.) may be suitable for this purpose.
[8] Macnaughtan, *J. Iron and Steel Inst.*, **109**, 409, 1924.
[9] O'Neill, *Carnegie Scholarship Memoirs, Iron and Steel Institute*, **17**, 109, 1928.
[10] O'Neill, *J. Iron and Steel Inst.*, **120**, 207, 1929.

features and provides for the making of vertical-motion static indentation tests as well as for translatory scratching tests.   The diamond is mounted in a tapered shank fitting into a vertical spindle, the bearing for which is fixed to a carriage capable of being moved upwards or downwards by operating a screw.   For indentation tests the specimen is laid on a horizontal table fitted to the inclined mechanical stage, and a suitable weight is placed on the platform at the top of the indenter spindle.   On turning the screw, the carriage, bearing, and weighted spindle steadily descend towards the specimen, and as the diamond makes contact with the latter the bearing drops away from the weight platform and the load is simultaneously applied. After the requisite period of application, the screw is turned in the opposite direction and the indenter is raised from the metal.

This provides one with an indentation machine capable of using very low loads and consequently of making extremely small impressions.   The latter prove to be very difficult to locate when required to be measured under the microscope, and if a series is being made, the author's method is to space them out in a straight line by using the micrometer stage of the scratch machine.   They are then ringed round with an inkmark, and placed on the mechanical stage of the measuring microscope, when the inkmark is quickly sighted.   The line of dints should soon appear and measurement is then commenced at one end of the line.   Results on two specimens are given in Table I.

TABLE I.—Micro-Brinell Tests with 1 mm. Diamond Ball.

Specimen.	Total Load. Kg.	Diameter, Microns.	Brinell Hardness Number.	"Ball Number" (P_m) Kg./mm.^{2}	
Cadmium VI (electro- deposit, 0·025 in. thick, on mild steel; ground, polished, and allowed to stand for two months)	0·065 *	86·0	11·2	11·2	Author's machine, 30 secs. loading.
	·085 *	93·5	12·3	12·4	
	·115	106	12·9	13·0	
	·165	120	14·6	14·6	
	·215	130	16·1	16·2	
	·315	147	18·5	18·6	
	·565	179	22·2	22·5	
	1·065	219	27·9	28·4	
	5·0 (standard)	404	37·4	39·0	Alfred Herbert machine.
Annealed 0·9 per cent. carbon steel (S 90)	0·165	52·2	75	77	Author's machine, 15 secs. loading.
	·315	54·7	134	134	
	·565	67·6	156	157	
	1·065	89·1	170	171	
	5·0	172	214	216	Alfred Herbert machine.
	30·0 (standard)	374	264	273	

The last column is obtained by dividing the load by the projected area of the indentation (πr^2) instead of the spherical area as required for the Brinell number.   This "ball number" is a more scientific value than the Brinell number and whilst being very much easier to calculate, does not differ greatly from the latter.   Its use is, therefore, to be recommended.

* At these loads, friction of the bearing is liable to play a part.

Reference to Fig. 1 will make it clear that some of the indentations reported above are sufficiently small to allow for the ball testing of metallic coatings 0·0005 inch in thickness. With very hard metals, however, the elastic recovery of the specimen will result in an indentation too shallow to be seen and measured under the microscope.

The well-known variation of Brinell number with testing load is only too evident in Table I., and the very low-load test would obviously require to be standardised before it could be of general utility. Indentations with a perfect conical tool should, give hardness numbers independent of the load—the reason for this is discernible in Fig. 1, where the cone and pyramid tools have a straight line relation between diameter and depth but the spherical tools have a varying ratio for these two quantities. Tests were therefore made with a smooth, "sharp"-pointed 120° diamond cone which was available mounted in a taper shank similar to that of the diamond ball.

TABLE II.—MICRO-INDENTATION TESTS WITH 120° DIAMOND CONE.

Specimen.	Total Load. Kg.	Diameter (Microns).	"Cone Number" P_m. Kg./mm.^{2}	Remarks.
Cadmium VI (electro-deposit, 0·025 in. thick, on mild steel)	0·065 *	72·5	15·7	} Imperfect impressions.
	·085 *	75·3	19·1	
	·115	77·3	24·5	
	·165	92·0	24·8	} Excellent impressions.
	·215	104	25·3	
	·315	123·5	26·3	
	·565	162·5	27·2	
Quenched 0·9 per cent. C. steel (100 S)	0·565	25·2 (?)	1130 (?)	} Very imperfect indentations.
	·765	27·4	1300	
	1·065	31·7	1350	

The results for the hardened steel are included not so much for their accuracy as to indicate what very small impressions can be measured, and how within limits the cone hardness number is reasonably constant. The 120° cone indentations are unduly deep for thin deposits, and a cone with an included angle of 168° 36′ might be tried. The depth of its indentations would be just one-twentieth of their diameter, and the static cone testing of coatings, one-thousandth of an inch in thickness, should be possible.

Scratch Testing.

Scratching has long served as a hardness test, and has lately been applied to electrodeposits. Whilst Sanigar[11] used a scratch machine designed by Professor C. H. Desch, most workers in the field have employed either the 90° cone Martens test or else the Bierbaum[12] apparatus. The scratches made by the latter are extremely small, although relatively deep, and the widths recorded for hard chromium deposits by the Grants[13] for instance, are only a few microns in magnitude. This necessitates the use of 2 mm. oil immersion objectives and magnifications of 1000 diameters.

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* At these loads, friction in the bearing is liable to vitiate the results.

[11] Sanigar, *Trans. Faraday Soc.*, **25**, I, 1929.

[12] Bierbaum, *Trans. A.I.M.E.*, **69**, 972, 1923.

[13] Grant, L. E., and Grant, L. F., *Trans. Amer. Electrochem. Soc.*, **53**, 509, 1928

Although Tables I. and II. indicate the possibility of conducting static indentation tests on thin coatings, the scratch test is nevertheless to be preferred in some respects. Scratches are much easier to locate for measurement than micro-indentations, and furthermore, in the case of the softer metals, for a given load and indenter a scratch is smaller than the impression produced by static indentation. This is owing to the shorter time that the moving tool is in contact with a given point on the surface of the specimen, and consequently flow of the metal does not take place to the same extent. A scratch also gives a better idea of the uniformity of the specimen, for it is really a very large number of adjacent indentations.

The author's scratch machine using the 1 mm. ball makes much wider scratches than those in the Bierbaum test, but they are relatively shallower. Loads of up to 1 kg. are employed, and the scratching operation is not difficult or particularly tedious, owing partly to the provision of a large mechanical stage on to which the test plate is rapidly affixed by clamps.
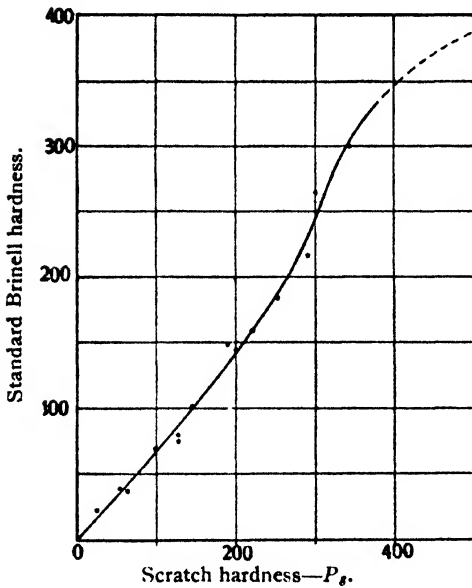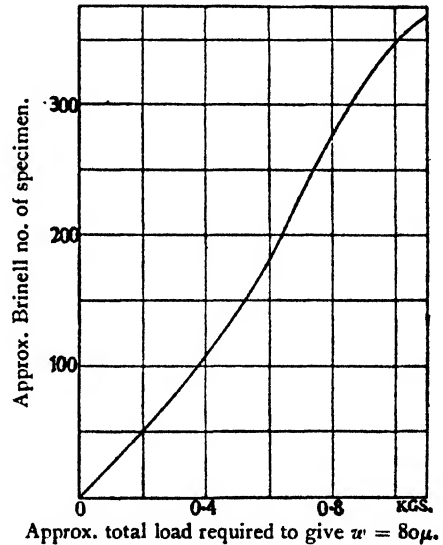

Fig. 2.

Fig. 3.

For thin light specimens a brass specimen holder carrying holding-down nuts and bolts fitting into inverted T-slots is used. A scratch about one centimetre long is ruled and width (w) measurements are made under the microscope with a Ramsden eyepiece by averaging five readings. Widths of much less than 0·050 mm. with 1 mm. diameter of curvature prove almost impossible to measure on the author's apparatus. The scratch hardness number is given by

$$P_s = \frac{8L}{\pi w^2} \text{ Kg. per sq. mm.}$$

where L is the total load on the diamond, including the spindle.

Tests have been carried out on various metals of known standard Brinell hardness number, and the results are given in Table III.

It may be observed in the last column of Table III. that for the particular conditions under which these tests are conducted, the scratch hardness number does not vary greatly with the testing load. As a scratch width of

TABLE III.—SCRATCH NUMBERS AND BRINELL NUMBERS.

Mark.	Specimen.	Brinell Hardness No.		Scratch Hardness.		
		Loading Conditions.	Brinell Number.	Total Load on Diamond (Kg).	Scratch Width (microns).	P_s Kg/mm.²
AA	Annealed aluminium (specimen AR recrystallised)	1 mm./5 Kg/ 30 secs.	23	·15	123	25
				·20	141	26
				·30	171	26
				·55	224	28
				1·05	296	30
Cd VI	Cadmium (polished electro-deposit ·025 in. thick)	1/5/30	37	·165	82	63
				·215	93·5	63
				·315	117	59
				·565	161	56
AR	Cold-rolled aluminium .	1/5/30	39	·15	84	54
				·20	99	52
				·30	122	51
				·55	166	51
				1·05	233	49
Brass I.	Soft brass sheet . .	1/10/30	69	·315	90	99
P 13 A .	Iron, decarburised and vacuum annealed .	1/10/120	69	·315	91	97
				·565	122	97
				·765	137	103
CUA	Electrolytic copper, etched	1/5/30	75	·30	77	129
				·55	110	115
				1·05	154	113
BW	Brass watch case . .	1/10/30	80	·315	79	128
CUD	Cold-drawn copper (CUA reduced 43 per cent.)	1/5/30	102	·30	72	148
				·55	103	132
				1·05	147	124
MV	Mild steel . . .	1/30/15	144	·215	53	195
				·315	64	196
				·565	85	200
P 13 R .	Cold-rolled iron (P 13 A reduced 59 per cent.)	1/10/120	148	·315	63	203
				·565	87	190
				·765	100	195
Brass II.	Cold rolled brass . .	1/10/30	159	·315	60	222
VRA	Annealed 0·4 per cent. C. steel	1/30/120	185	·55	75	250
				1·05	110	221
VR	Cold rolled 0·4 per cent. C. steel	1/30/120	216	1·05	96	290
S 90	Annealed 0·9 per cent. C. steel	1/30/120	264	·565	69	305
				·765	81	300
D 5	Chromium steel-tempered	1/30/15	300	·565	65	340
				1·065	89	343
D 9	Chromium steel . .	10/3000/15	401	·765	59	560
		1/30/15	390	1·065	69	570

o·080 mm. is comfortable to measure, this size has been adopted as a rough standard, and the use of a load on the machine to produce this amount of deformation is recommended where the thickness of metal permits. Fig. 2 has been drawn up on this basis, and should enable one to determine very approximately, the Brinell number of a specimen which has been tested on the scratch machine. Similarly, Fig. 3 will serve as a guide to the selection of a testing load if one knows, or can judge, the approximate Brinell number of the metal.

Scratch Tests on Cadmium of Various Thicknesses.

To make sure that thin deposits could be tested with reliability, a series of soft cadmium electro-deposits of various thicknesses was obtained. These were kindly prepared by Mr. L. Davies of Messrs. Metropolitan-Vickers, Ltd., Manchester, and were plated with a current density of 6 amps. per sq. ft. on to smooth mild steel cathodes 0·066 inch thick, of uniform composition. The surfaces were scratch-tested as deposited, and without any preparation other than cleaning with selvyt and " Silvo." A specimen of the unplated cathode was also tested after rubbing on ooo emery paper. As this basis metal was much harder than the cadmium deposits, the object of the tests was to determine the thickness at which it began to influence the results. This can be seen in Table IV.

TABLE IV.—CADMIUM OF VARIOUS THICKNESSES ON STEEL. SCRATCH WIDTHS (w) IN MICRONS.

Total Load on Diamond. Kg.	Steel Cathode. No Deposit.		Deposit V. 0·001 in. Cd.		Deposit IV. 0·00075 in. Cd.		Deposit III. 0·0005 in. Cd.		Deposit II. 0·00025 in. Cd.	
	w.	P_s.	w.	P_s.	w.	P_s.	w.	P_s.	w.	P_s.
0·115	—	—	58	87	58	87	58	87	57	90
·165	—	—	71	83	72	81	71	83	64·5	101
·215	53	195	82	81	84·5	77	84	78	69	115
·315	64	196	102	77	104	74	103	76	90·5	98
·565	85	200	142	72	142	72	141	72	127	90
Micro-Brinell test, 0·085 Kg. 30 secs.	—	—	87	—	87	—	85	—	85	—

Results lying above the thick black line in Table IV. should be reliable from the point of view of scratch width and thickness of coating. The first scratch for Deposit II. has a width of 0·057 mm., which according to the 1 mm. ball curve in Fig. 1 should be suitable for a minimum thickness of 0·0056 mm. (0·00022 inch). It should, therefore, just be feasible to scratch Deposit II. accurately with the 0·115 Kg. load but not with higher loads. The experimental results bear this out, and the instrument in this case is successfully testing a 0·00025 inch coating. Whilst Table IV. confirms a thickness factor of seven times the indentation depth, it is rather

curious that the results for the 0·565 kg. load on Deposits III., IV., and V. should be so low and apparently uninfluenced by the hard steel backing metal.

TABLE V.—TESTS ON DEPOSITS 0·020 MM. THICK.

Specimen.	0·215 kg. Load.		0·315 kg. Load.		·565 kg. Load.		Approx. Brinell Nos. from Fig. 2.	MacNaughtan's Brinell Results.[1]
	w.	P_s.	w.	P_s.	w.	P_s.		
Lead on copper sheet; unpolished.	264	7·8	—	—	—	—	5	3 – 5
Tin on copper sheet; unpolished.	152	24	—	—	—	—	16	—
Cadmium on copper sheet; polished.	104	51	126	50	—	—	33	12 – 53
Zinc on copper; polished.	—	—	109	67	147	67	43	40 – 50
Copper on iron; unpolished.	—	—	92	94	—	—	60	58 – 150
Nickel on copper; polished.	—	—	83	117	123	95	Results unreliable. Cathode too soft.	—
Iron, 0·004 in. thick, stripped from cathode								
(*a*) unmounted.	—	—	57	246	? (96)	(156)	—	167 – 350
(*b*) mounted on glass.	—	—	59	231	? (95)	(160)	170	—

TABLE VI.—NICKEL DEPOSITS ON STEEL.

Particulars of Plating Bath.	Scratch Width, w Microns.	P_s. kgs./mm.[2]	Approx. Brinell No. from Conversion Curve.
Ni. sulphate . 250 g./lit. ⎫ Ni. chloride . 3 „ ⎬ Boric acid . 25 „ ⎭ Sod. fluoride . 1·5 „	95	216	155
Ni. Am. sulph. 62·5 „ ⎫ Ni. sulphate . 31·25 „ ⎬ Boric acid . 15·6 „ ⎭ Sod. chloride . 15·6 „	82·5	287	225
Ni. sulphate . 80 „ ⎫ Am. „ . 20 „ ⎬ Pot. chloride . 8 „ ⎭	77	329	290

Thickness, 0·00075 in.   Testing load, 0·765 kg.

Solution with—			
Sodium fluoride ¼ oz./gall.	65	340	300
„ ½ „	70	294	235
„ 1 „	71	286	230
No fluoride	91	173	120

Thickness, 0·001 in.   Testing load, 0·565 kg.

The micro-Brinell figures in Table IV. are given solely to demonstrate that a static test (with a warm indenter) on a soft metal like cadmium gives much deeper impressions than those produced during the scratch test by an equally loaded but moving diamond.

Tests on Commercial Deposits.

Table V. gives results of electrodeposits on cathodes of thin sheet metal. With these materials the small brass specimen holder was always employed, except in the second tests of the iron strip (detached from its cathode). Much lighter loads should have been used for the lead and the tin, and the hardness values for these metals are probably high.

Table VI. records tests on nickel deposits prepared from various solutions by Messrs. Metropolitan-Vickers, Ltd.

Tests on coatings and deposits of this type present no difficulties, but if the metal is much harder than 400 Brinell, then measurement of the scratch becomes a problem. It is probably not desirable to increase the maximum load already used on the indenter, and the alternative of reducing the size of the latter is suggested. It seems likely that a polished hemispherical diamond of $\frac{1}{2}$ mm. diameter of curvature would prove to be a more suitable tool in every way, and the author is assured that the production of such indenters is quite a straightforward operation.

Summary.

The factors involved in the hardness testing of thin metallic coatings have been analysed, and the advantages and limitations of scratch tests discussed. A machine designed by the author for other work, and using a 1 mm. hemispherical indenter has been found snitable for the indentation and scratch testing of coatings down to less than 0·0005 inch in thickness, provided that they are not much harder than about 400 Brinell. An empirical conversion curve for obtaining approximate Brinell numbers from scratch hardness numbers has been prepared. It is suggested that a $\frac{1}{4}$ mm. diamond hemispherical indenter on a machine of the same general type would be of still greater utility, as harder deposits could then be tested.

Scratch tests are recorded made on nickel deposited from baths of different compositions.

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THE EFFECT OF STIRRING ON THE RATE OF COAGULATION OF GOLD SOL.

By EMLYN JONES.

The main object of the present investigation has been to determine what effect stirring has on the rate of coagulation of a gold sol, the coagulation being brought about by the addition of electrolyte. The effect is followed by determining the value of the coefficient β in the equation of Smoluchowski,[1] *viz.*,

$$\beta = \frac{1}{t}\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right).$$

[1] Smoluchowski, *Z. physik. Chem.*, **92**, 129, 1917

In this expression v_0 is the initial number of primary particles, v_1 the number of such particles remaining after time t. Several investigators have put this equation to the test. They find, especially after a preliminary treatment designed to control the thermo-senescence effect,[2] that the above equation holds reasonably well when the region employed approximates to rapid coagulation. During slow coagulation, however, there is a marked decrease in the value of the coefficient β.

In the present work the equation is used as a means of comparing the rate and extent of the coagulation.

In connection with the effects produced by stirring, Smoluchowski[1] showed, from theoretical considerations, that, with increase in particle size, the collision of particles, caused by the streaming or convection currents during stirring, became more important than that due to the Brownian Movement. He considered a stationary particle and calculated the ratio of the number of particles which enter the sphere of attraction on account of stirring to those which arrive of their own account, *i.e.* by their Brownian Movement. From the formula thus derived he concluded that, while stirring has only a small effect on coagulation in the case of amicrons and submicrons its influence becomes very considerable with larger particles.

The effect of stirring on the coagulation of CuO and other sols has been observed by Freundlich and Basu.[3] The most evident action of stirring in this work was its promoting and accelerating influence. They observed that the velocity of coagulation was increased by stirring in cases in which (*a*) the concentration of the coagulating electrolyte was large, and (*b*) a strongly coagulating ion was employed. In the case of gold sol, however, a retarding effect on the coagulation was observed when employing a small concentration of electrolyte and moderately strong coagulating ions. No quantitative results were, however, obtained. The explanation given was, that, as a consequence of stirring, the secondary and tertiary particles which were first formed were always split up again ; they therefore did not agglomerate so quickly to the size at which the coagulation was favoured by the stirring.

Freundlich and Kroch [4] have studied the coagulation of a CuO sol by stirring alone. Ostwald [5] has attempted to give a theoretical explanation of these results based on the conception that a stirring apparatus could produce an electrical potential difference in various ways, the charges so produced being supposed to influence the actual coagulation process. Such a view, however, as pointed out by Freundlich and Loebmann,[6] stood in contradiction to certain observations made by them, for instance, the fact that the ζ-potential of the partly coagulated sol after centrifuging was the same as that of the sol before coagulation. Freundlich and Loebmann [6] extended the investigation to goethite sols FeO(OH). They found that the sol could be coagulated by an air current, shaking with quartz or with organic liquids, *e.g.* benzene. Mechanical coagulation appeared to be the result of an enlargement of the surface of contact. The work was discussed in the light of Deutsch's [7] explanation of coagulation at an interface.

In a still more recent paper, Freundlich and Loebmann [8] have shown

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[2] *Cf.* Miss A. Davies, *J. Physical Chem.*, **33**, 274, 1929; P. J. R. Butler, *ibid.*, **34**, 656, 1930.

[3] Freundlich and Basu, *Z. physikal. Chem.*, **115**, 203, 1925.

[4] Freundlich and Kroch, *ibid.*, **124**, 155, 1926.

[5] Ostwald, *Kolloid. Z.*, **41**, 71, 1927.

[6] Freundlich and Loebmann, *Z. physikal. Chem.*, **139**, 368, 1928.

[7] Deutsch, *ibid.*, **136**, 355, 1928.

[8] Freundlich and Loebmann, *Kolloid-chem. Beihefte*, **28**, 391, 1929.

the improbability of some of the attempts made to explain mechanical coagulation. According to them the most likely explanation is that coagulation takes place at the surface of the solution where a certain orderly arrangement of particles may exist. Mechanical agitation effects a constant change of surface. The surface need not be sol-air interface. The experiments carried out show that the effect is produced at any surface provided by a medium of low dielectric constant whether it be gas, liquid or solid. The influence of electrolytes at small concentrations under the threshold value for coagulation was diminished by stirring.

The rate of coagulation of ferric oxide sols by KCl at the ordinary temperature has been followed spectrophotometrically at different rates of stirring by Jabltzynski and Szames.[9] The results were taken as indicating that stirring produced an increased frequency of collision between the primary particles followed by the mechanical disruption of the larger aggregates produced during the first stage. Butler[2] and other investigators of this Laboratory, working with gold sol in the " rapid " region of coagulation, found that shaking, by hand, produced a marked increase in the velocity of coagulation.

The present investigation was undertaken as the outcome of these results. The apparatus, to be described, allowed of a stricter control of the stirring conditions than that exercised by the workers referred to. The concentration of barium chloride, used as coagulating agent, and also the rate of stirring could be varied at will and the effects so produced on the rate of coagulation, investigated.

Experimental.

The gold sols used in the investigation were prepared by the "acetone" reduction method previously employed by Miss Davies.[2] The sols were dialysed in collodion membranes for three days, the distilled water being renewed twice a day. Prior to use all sols were brought to a stable and reproducible state by subjecting them to heat treatment at 80° C. for three hours as recommended by Miss Davies and by Butler. Redistilled water, obtained by the redistillation of ordinary distilled water from silver lined copper vessels, was employed in making up the various solutions. All vessels and stirrers were of quartz. It may be emphasised here that particular care was taken to obtain thoroughly clean vessels and stirrers. This was carried out by treating first with hot NaOH, alcohol-nitric acid mixture, distilled water and redistilled water, the vessels being finally steamed out for five minutes with steam from redistilled water.

The *original* gold sol, after dialysis, contained about 56 mgs. of gold per litre. In the present investigation the sol was diluted with redistilled water in various proportions. Owing to the increased spatial separation of the colloid particles brought about by diluting the sol, the speed of colour change was diminished and therefore made easier to follow.

Apparatus.—In order to be able to follow exactly the influence of stirring it is necessary that certain experimental conditions be fixed from the beginning, otherwise the values obtained are not reproducible and comparable. The influence of stirring is not only dependent on the speed of the stirring but, *e.g.*, on the quantity of liquid rotated, on the kind and size of stirrers employed, on the diameter of the vessel, etc. At first an apparatus similar to Butler's[2] was tried, the only modification being the introduction of the stirrer. It was, however, found to be unsuitable for the problem in

⁹ Jablczynski and Szames, *Bull. Soc. chim.*, (iv.), **45**, 206, 1929.

hand. The same quartz apparatus was, however, employed but the means of introducing the $BaCl_2$, used to initiate the coagulation process, and the gelatin, used to arrest the process, was modified. The two small vessels containing the electrolyte and gelatin solutions in Butler's apparatus were replaced by straight pieces of glass tubing, diameter about $\frac{1}{4}$ inch, and a length of 4 to 5 inches. These tubes were fitted into corks which in turn fitted into the necks of the quartz flask containing the sol. Each tube was, therefore, in a vertical position, one end of each tube being inside the flask and above the sol. Attached to the other or " free " end of the tubes were pieces of rubber tubing closed by spring clips. The electro-lyte and gelatin solutions, contained up to a certain constriction mark made in each of these tubes, could be easily released into the sols by merely opening the clips, such a procedure taking only a fraction of a second. A piece of rubber tubing closed by a spring clip was attached to the side tube of the quartz flask. One second previous to the addition of the electrolyte and gelatin solutions this clip was opened to the air in order to facilitate the flow of these solutions from their respective container tubes. The clip was closed immediately after the delivery.

The volume of a known concentration of $BaCl_2$ solution delivered by the container tube was found both gravimetrically and volumetrically. The two methods gave concordant values, namely 2·50 c.c. From the know-ledge of the normality of the $BaCl_2$ employed and the volume introduced, the concentration of electrolyte in the sol itself may be calculated.

The apparatus (compare Butler),[2] therefore, consisted of a quartz flask carrying three necks and a side tube. The central neck was about $\frac{3}{4}$ of an inch in diameter and of sufficient width to allow of the passage of the paddle stirrer. Fitting into this neck by means of a ground joint was a quartz guide for the stirrer. Evaporation of the sol was reduced to a minimum by having a mercury seal between stirrer and guide. The stirrer was rotated by means of an electric motor, the speed of which could be regulated. The number of revolutions per minute made by the stirrer rod was ascertained by means of a revolution counter attached to its axle. The stirrer itself was completely immersed in the sol being a few millimetres from the bottom of the vessel. With the two-bladed paddle type of stirrer the liquid surface during the stirring was almost a hollow sphere and at moderately high rotations numerous small bubbles were formed in the locality of the stirrer. In order to prevent as far as possible any motion of the sol due to external vibration, the flask and stirrer guide were kept rigid by clamping to the side of the thermostat the temperature of which was kept constant at 25° C.

In order to conduct a stirring experiment, the following was the method adopted :—

100 c.c. of the diluted sol were placed in the quartz flask ; the tubes, one filled with a definite volume of $BaCl_2$ solution of known strength and the other with a 2 per cent. gelatin solution, were placed in the two outer necks of the quartz flask. The stirrer and guide were then fixed into the central neck and the whole placed in the thermostat at 25° C. and left for 15 mins. to attain this temperature. The stirrer was then rotated at a known rate and the electrolyte introduced at a known moment of time by opening the spring clip of the container tube and in this way initiating the actual coagulation process. At the end of the arbitrary time allowed for coagulation the gelatin solution was added, thus preventing further coagu-lation as recommended by Zsigmondy.[10]

[10] Zsigmondy, *Z. physikal. Chem.*, **92**, 600, 1917.

The coagulation of a gold sol involves a colour change from red to blue, the red colour being assumed to be due entirely to primaries. The percentage red, which is proportional to the amount of uncoagulated sol is determined by Hatschek's [11] colorimetric method, a full description of which is given in his own paper. The modifications introduced by Miss Garner,[12] and by Butler[2] for dilute sols, were utilised in the present investigation.

Results.

In the following tables the β values, obtained for different rates of stirring and for different periods of coagulation, are tabulated. The period of coagulation "t" refers to the time interval between initiating and arresting the coagulation process.

Table I. is a typical example of the results obtained when the concentration of the $BaCl_2$ solution *in the sol* is such as to ensure "rapid" coagulation, this concentration being $0.0081N$. The sol is so diluted as to contain about 28 mgs. of gold per litre. In this table t is expressed in seconds and β calculated on that basis.

TABLE I.—(SOL. 11).—REGION OF RAPID COAGULATION.

Rate of Stirring (Revs. per Minute).	0.	80.	200.	400.	600.	1000.	1400.
$\beta \times 10^{-2}$ when $t = 5$ seconds	3·90	6·66	7·92	9·60	9·80	10·02	9·60
$\beta \times 10^{-2}$ when $t = 10$ seconds	3·45	4·51	4·90	6·30	7·54	8·26	8·90
$\beta \times 10^{-2}$ when $t = 15$ seconds	3·41	5·03	5·25	—	6·35	6·67	6·67

Table II. is a typical example of the results obtained when the concentration of the $BaCl_2$ in the sol, namely $0.00081N$, is such as to give rise to conditions of slow coagulation. The sol employed contains about 28 mgs. of gold per litre.

TABLE II.—(SOL. 28).—REGION OF SLOW COAGULATION.

Rate of Stirring (Revs. per Minute).	0.	100.	200.	400.	600.	1000.	1400.
$\beta \times 10^{-1}$ when $t = \frac{1}{4}$ min.	6·06	5·01	4·14	3·66	3·66	3·24	3·24
$\beta \times 10^{-1}$ when $t = \frac{1}{2}$ min.	3·88	3·48	3·48	3·08	2·88	2·88	2·54
$\beta \times 10^{-1}$ when $t = 1$ min.	3·05	2·64	2·40	2·40	—	1·94	1·94
$\beta \times 10^{-1}$ when $t = 2$ mins.	2·16	1·74	1·74	1·45	1·32	1·32	1·32

In the above Table t is expressed in minutes and β calculated on that basis. Figures 1 and 2 correspond to Tables I. and II. respectively and are obtained by plotting β against the rate of stirring—in revolutions per minute—at the various periods of coagulation employed during an experiment.

[11] Hatschek, *Trans. Faraday Soc.*, 17, 499, 1921.
[12] Miss Garner, *J. Physical Chem.*, 30, 1404, 1926.
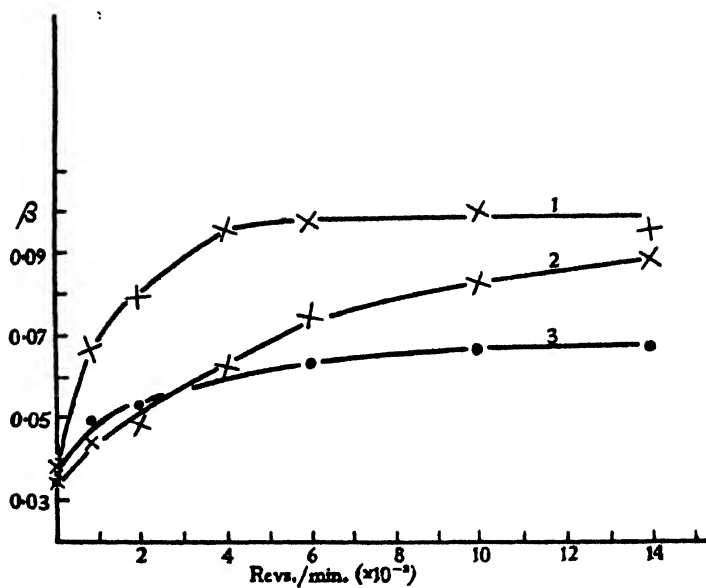
1. $t = 5$ secs.   2. $t = 10$ secs.   3. $t = 15$ secs.
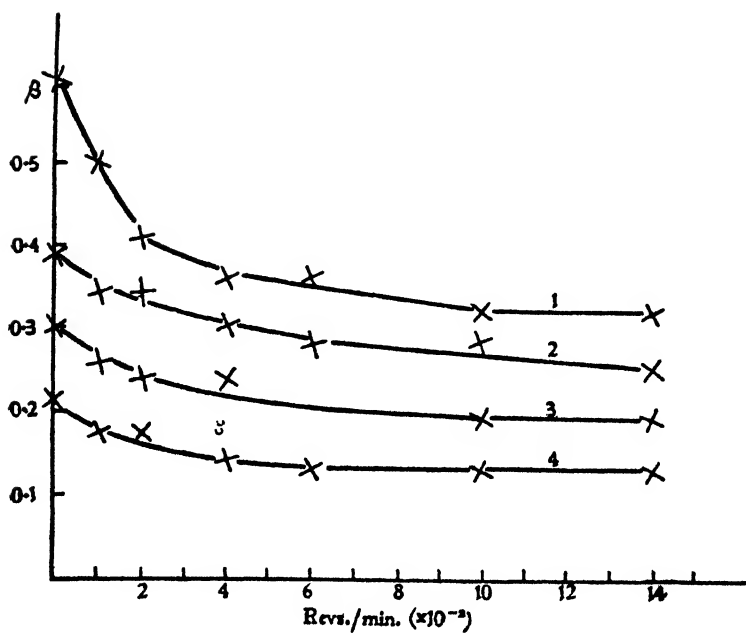
Fig. 1.

1. $t = 10$ secs.   2. $t = 30$ secs.   3. $t = 60$ secs.   4. $t = 120$ secs.

Fig. 2.

Discussion of Results.

When working in the region of rapid coagulation the writer has found in the cases examined that the constancy of β is fair, when no agitation of the sol takes place. The results may be taken as indicating that the Smoluchowski equation is holding in this particular region.

When the sol is stirred the curves depicting the rate of coagulation show an increase in the β value as the intensity of the agitation increases. This is true for each period of coagulation. The greater the number of revolutions per minute to which the stirrer is subjected, the greater becomes the value of β. In the majority of cases the β values reach limits which remain constant, or nearly so, for all higher rotations.

In the region of slow coagulation (Table II.) the concentration of $BaCl_2$ is not sufficient to give rise to completely discharged particles ; the sol particles are, therefore, characterised by a residual charge. When the sol is not agitated the β values decrease as the coagulation proceeds, i.e., at a low electrolyte concentration coagulation takes place more slowly than the Smoluchowski theory demands. This agrees with the observations of previous workers.

In this region of colloid coagulation it is very evident, from the experimental values and the shape of the curves arising from them, that stirring has a decided inhibitive or retarding effect on the slow coagulation of a gold sol.

The two regions will now be dealt with in more detail.

Region of Rapid Coagulation.—It may be noticed, from the short survey of the literature given in the introductory portion of this paper, that the most evident effect of stirring is its promoting and accelerating influence on coagulation.

Owing to the complex nature of the results obtained in the present investigation, it is, however, difficult to arrive at any definite conclusions with regard to the explanation of such results.

It may be recalled that, according to Smoluchowski, while stirring has a small effect on coagulation in the case of amicrons and submicrons, its influence becomes very considerable with larger particles.

Although stirring may, therefore, produce an increase in the number of collisions between sol particles, the writer believes that there is another factor which may account, partly at least, for the increase in the rate of coagulation by stirring. This is aeration or the formation of air-bubbles in the sol. The formation of bubbles is increased by increasing the violence of the stirring. They are formed in the vicinity of the stirrer. According to Edser [13] when two solid particles, suspended in a liquid, are brought sufficiently near to each other, attraction—real or apparent—may occur if minute air bubbles are present in the liquid and the angle of contact between the liquid and solid is greater than zero. In this way a number of particles may adhere to a bubble or a number of bubbles may form connecting links between numerous particles.

It will be appreciated readily that a bubble moving about in a liquid has an opportunity to collect particles which are too widely dispersed to exert any attraction, real or apparent, on each other. Obviously, however, further experimental work will be required to examine the quantitative influence of such an effect.

Region of Slow Coagulation.—In the present investigation stirring

[13] Edser, *Inst. Min. Met.*, **29**, 190, 1920.

has been found, in this region, to have a definite retarding or inhibiting *effect on the ordinary course of coagulation.* This agrees *with certain ob-*servations made by Freundlich and Basu.[3] The explanation given by them is that stirring produces a disaggregation of the secondary and tertiary particles which are first formed. This inhibitive effect of stirring may, therefore, have its origin in the fact that the agitation produces convection currents in the form of violent eddies, which might have some kind of shearing effect on the particles causing complete or partial splitting-up or disruption of the particles.

The writer believes, however, that the following explanation is of a more satisfactory nature than the above.

The region of slow coagulation differs from the rapid in that the particles possess a residual charge and are thus characterised by an incomplete electrical double-layer. Owing to the various forces set up by the stirring a displacement of the outer layer may occur, resulting in the further exposure of some of the charge on the particles. This would mean a temporary but effective increase of charge on the colloid particles and, therefore, a decrease in the coagulation velocity. Such a displacement could be more readily imagined if the outer layer be considered as diffuse, as has been done by Gouy.[14]

Summary.

1. Employing an apparatus which ensures more controllable conditions of stirring than those obtained by previous investigators, the effect of agitating the sol, when in process of coagulation by various concentrations of electrolyte, is investigated.

2. The results obtained are very complex. When the concentration of electrolyte is such as to ensure conditions of rapid coagulation, stirring produces a decided accelerating influence. Such an accelerating effect is attributed not simply to the increase in collision frequency between the particles of the sol, but likewise to the aeration or formation of air bubbles in the sol. The conditions existing in such aeration are likely to be favourable to aggregation.

3. When the concentration of electrolyte is such as to give rise to slow coagulation of the gold sol, stirring is found to have a retarding or inhibitive effect on the coagulation. This may be accounted for by a disruption or displacement of the "imperfect" or incomplete outer layer of the double layer, giving rise to temporary but effective increase of charge and, therefore, to a decrease in coagulation velocity.

[14] Gouy, *Ann. Physik,* (9), **7**, 129, 1917.

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VAPOUR PRESSURE AND HEAT OF DILUTION.—PART VII. VAPOUR PRESSURES OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AND OF ALCOHOLIC SOLUTIONS OF CALCIUM CHLORIDE.

By Aileen M. Hayward and E. P. Perman.

Method.

The apparatus used here for the determination of vapour pressures was a modified form of that devised by Downes and Perman,[1] and the principle employed was the same.

In the experiments by previous workers it was considered that the errors due to impurities in the air, such as carbon dioxide, sulphur dioxide, hydrogen sulphide, etc. were negligible. This was not the case with the solutions investigated here, and it was essential that the air should be free from all traces of Carbon Dioxide, which would react with the Sodium Hydroxide. This was ensured by passing the air through a train consisting of two U-tubes, the first containing granular soda lime, and the second, small pieces of caustic soda. These tubes were refilled frequently.

The Saturator.—The air passed from the purifying train into four saturating bulbs in the thermostat. The first was made of a glass which was shown by experiment to be resistant to the action of caustic soda. The last three were made all in one piece of pure silver, the makers being Walker and Hall, Sheffield. It was essential that they should be of pure silver to ensure that the solutions should be free from all traces of silicates which would be formed by the action of the strong caustic soda solutions on glass at the high temperatures of the experiments. The shape of the bubblers ensured that the air in passing through stirred the liquid very efficiently.

It was shown by Perman that sufficiently complete absorption could be obtained with three bulbs, but that the concentration of the solution in the last one might vary slightly. Four bulbs were therefore used to ensure that the saturated air left a solution of known concentration. The quantity of solution in the four bulbs was 120 c.c., and the weight of vapour collected in the absorption bubblers was never more than 0·5 grams in one experiment. The air was passed through at the rate of about one litre per hour, and never as rapidly as two litres per hour. Experiments with much slower air currents gave results identical with those obtained at the usual speed. This showed that saturation was complete at that speed.

Great difficulty was experienced in obtaining efficient glass-silver joints between the silver bubblers and the glass bulb at one end, and the equilibrium tube at the other. The joints were finally made by having a glass tube of slightly greater diameter fitting right over the silver tubes; the whole joint was covered with thick pressure tubing, and the ends first wired

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[1] *Trans. Far. Soc.,* **23,** 95, 1927.

and then well covered with shellac. It was found that at the lower temperatures this was perfectly satisfactory, but at temperatures above 60° C. the heat rendered the rubber spongy, and it had to be renewed frequently.

The silver bubblers were filled by connecting the outlet tube of the bubblers to the outlet tube of the vessel containing the solution, and applying suction at the inlet end of the bubblers. This was continued until the level of the liquid just appeared above the inlet tube. By comparison with similar glass bubblers, it was known that, when filled in that way, the inlet tubes of the bulbs dipped 1 cm. below the surface of the liquid in the bulbs.

Vapour Pressures of Aqueous Solutions of Sodium Hydroxide.

Previous Work.—Very little has been done on the vapour pressures of solutions of sodium hydroxide in water, although the determinations would be of value. Gerlach [2] obtained the boiling-points of sodium and potassium hydroxide solutions of various concentrations. Tamman [3] gave the vapour pressures of solutions of sodium hydroxide of different strengths at 100° C., the highest concentration used being 75 grams of hydroxide to 100 grams of water. Dieterici [4] obtained the vapour pressures of solutions of sodium hydroxide, potassium hydroxide and calcium chloride at 0° C. A fairly extensive series of measurements was made by Wüllner,[5] who investigated the vapour pressures of solutions of sodium and potassium hydroxides of two concentrations, over a range of temperature from 10° C. to 100° C. He used a static method, in which the solution to be investigated was introduced into the vacuum over a "shortened barometer column," and the pressure so obtained. This method is recognised as incapable of producing accurate results, owing to the inherent difficulties of manipulation, and to the difficulty of removing all air from the barometer column and the solution. A further error would be introduced in this case, as the tubes were necessarily made of glass; this would result in the presence of traces of silicates in the solutions. A comparison of the results obtained by Wüllner with those by Paranjpe, and in the present work, indicates that those of Wüllner are considerably higher than the other values.

The most complete series of vapour pressure measurements was made by Paranjpe,[6] who investigated concentrated solutions of sodium hydroxide at the temperatures 0°, 10°, 20°, 30° and 40° C. He used the static method in which air-free liquid is in equilibrium with its own vapour, and although the results are in fair agreement with those of the present work, several objections might be raised to the procedure. The solution was introduced into a small vessel, contained in a Dewar flask; the air was removed by freezing the solution in alcohol cooled in liquid air, and pumping off the residual gases. While this would be effective for solutions of low concentration, the strong caustic soda solutions are extremely viscous, and in the work under discussion contained large quantities of solid sodium carbonate, so that the complete removal of the air would be doubtful. The caustic soda used in the work contained as much as 2 per cent. of sodium carbonate; the effective concentration of the solutions was estimated by titration, with methyl orange as indicator, the total alkali present being estimated as sodium hydroxide. The Dewar flask was provided with an electric heater and stirrer, but no regulator was used; Paranjpe states that

[2] *Z. analyt. Chem.*, **26**, 413, 1887.   [3] *Mem. Acad. Peterb.*, **7**, 35, 1887.
[4] *Wied. Ann.*, **42**, 1891; **50**, 1893; **62**, 1897.   [5] *Pogg. Ann.*, **110**, 1860.
[6] *J. Indian Inst. Science*, **2**, 1916.

the temperature was constant to approximately $0.1°$, but this is not sufficiently accurate for work on the vapour pressures. The method is admittedly very limited in its application, as for vapour pressures greater than 23 mms. of mercury no experiments were possible owing to distillation. It is doubtful whether it is accurate for pressures somewhat below this limiting value. The pressures given by Paranjpe for low concentrations were obtained by extrapolation.

A table of comparison of our results with those obtained by Paranjpe at 30° C. and by Wüllner [5] is given (Table I.); this is the only temperature at which this is possible, but the comparison of the results of Paranjpe with those of other workers at 0° C. indicates that his results at that temperature are usually low. At 30° C., however, it can be seen that his results are for the most part in good agreement with those of the present work.

TABLE I.—COMPARISON OF THE RESULTS OBTAINED FOR THE VAPOUR PRESSURES OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AT 30° C.

G. per 100 g. Solution.	Vapour Pressure in mm. of Mercury.		
	A.	B.	C.
10	27·32	27·52	—
16·6	25·04	25·24	26·0
20	23·12	23·16	—
23	20·76	20·76	22·4
28	16·32	16·00	—
32	12·80	12·40	—
36	9·64	9·28	—
40	6·68	6·88	—
44	4·96	4·88	—
48	3·60	3·36	—

The references are: A. Miss Hayward and Perman; B. Paranjpe [6]; C. Wüllner.[5]

Experimental Procedure.—Of several samples of sodium hydroxide examined, the purest was found to be that obtained from Hopkin & Williams; it contained 99·13 per cent. of the hydroxide, and all the impurity was sodium carbonate. The carbonate was removed from solution by precipitation with standardised baryta. The caustic soda was weighed out exactly in making up a solution, and added quickly to well-boiled distilled water. The purity of the caustic soda being known, the exact amount of baryta was added to precipitate the carbonate present, the barium carbonate formed being allowed to settle before filling the bubblers. The presence of small amounts of solid in the bubblers was found to have no effect on the vapour pressure of the solutions.

In the early experiments the solutions were prepared in a glass bottle. The effect of the strong alkali on the different makes of glass was first ascertained. Samples were weighed, boiled for half an hour with strong sodium hydroxide solutions, rinsed, dried and reweighed. Soda glass proved very resistant, the bottle used losing weight only very slightly on the first treatment, and the loss on subsequent treatments being negligible. Pyrex glass was found to be very readily corroded by the strong alkali, the surface after treatment being rough, while there was an appreciable loss of weight.

In the later experiments a pure silver flask was obtained for preparing the solutions; this was fitted with a rubber stopper having two holes, through one of which passed a tube containing soda lime, and through the

other a tube used in filling the bubblers, which reached to the bottom of the flask.

The strength of the solutions was accurately ascertained by titration with carefully standardised hydrochloric acid, using phenolphthalein as indicator. As it was essential that the weight-concentration and the volume-concentration of the solutions should be known, a study of the densities of the solutions over a wide range of concentration at the temperatures of the experiments was also undertaken. The densities were measured using a bottle of 25 c.cs. capacity, having a very narrow neck. The bottle was first well boiled with a strong solution of caustic soda, washed with distilled water, and then dried and weighed. It was standardised at each temperature. The solutions were allowed to stand for days in air-tight bottles until absolutely clear before introducing them into the density bottle. It was found that the strongest solutions remained cloudy even after standing for weeks ; these were therefore filtered, using a Gooch crucible previously well boiled with alkali.

The tables of results for the five temperatures of the experiments, namely 30°, 45°, 60°, 70°, and 80° C., are given, and the graphs of vapour-pressure-concentration and of density-concentration plotted from these. The vapour-pressure-concentration curves for each temperature show a definite point of inflection ; in this they resemble the curves obtained by Harrison and Perman [7] for aqueous solutions of calcium chloride. The similarity in the shape of the curves given by these two substances was expected from the fact that they are both strongly ionised in solution and are both hydrated in solution. In the case of caustic soda, however, the double flexure is very much more marked, since it is a much stronger electrolyte. The flexure at high concentrations may be ascribed to decrease in ionisation, or to decrease in hydration, or to both these causes. The shape of the curve at 60° C., which is the transition curve between the very steep curves at 80° and 70° and the flatter ones at 45° and 30°, appeared slightly different from the others, and the curve was, therefore, repeated ; the new points were found to lie exactly on the previous curve.

The curves show great depression of vapour pressure, e.g., at 80° C. the depression is from 354·8 mms. to 16·50 mms. The lowest vapour pressure measured was 3·14 mms. at 30° C. The accuracy of the method is such that, even with these low pressures, the agreement between the two results at the same concentration was good. At each temperature the solutions investigated ranged from a dilute solution to near saturation ; in no case were crystals deposited in the bubblers during an experiment, but at the higher concentrations the majority of the solutions were supersaturated at room temperature, and the whole of the solution crystallised to a solid mass immediately on removal from the thermostat. This made manipulation more difficult at high concentrations, but did not affect the actual vapour pressure determinations.

In general, two determinations of the vapour pressure were made with each solution to ensure accuracy. Table II. shows the results for each temperature ; the concentration is expressed in three ways : (1) Grams of solute per 100 grams of solution ; (2) Grams of solute per 100 c.cs. of solution ; (3) The ratio of the number of solute molecules (n) to the number of solvent molecules (N) present in the solution. The mean of the two values obtained for the vapour pressure of each solution is given, together with the density.

[7] *Trans. Faraday Soc.*, **23**, 72, 1927.

TABLE II.—Vapour Pressures and Densities of Solutions of Sodium Hydroxide in Water.

Temperature °C.	Concentration (g./100 g.).	Concentration (g./100 c.cs.).	$\frac{n}{N}$	Density.	Vapour Pressure.
30	12·84	14·55	0·06485	1·1329	26·80
	18·87	22·62	·1046	1·1988	23·88
	26·28	33·59	·1604	1·2782	17·85
	33·28	45·04	·2245	1·3537	12·10
	38·32	53·70	·2796	1·4016	7·97
	43·02	62·35	·3398	1·4492	5·42
	49·91	75·48	·4483	1·5124	3·16
45	10·03	11·03	0·0502	1·0985	64·65
	20·81	25·24	·1182	1·2128	50·18
	25·37	31·99	·1530	1·2614	42·50
	33·70	45·47	·2294	1·3494	27·14
	38·16	53·19	·2776	1·3939	19·67
	44·28	63·83	·3575	1·4415	12·35
	51·21	77·34	·4723	1·5104	7·78
	56·43	87·64	·5826	1·5534	5·106
60	8·993	9·716	0·04447	1·0804	136·4
	9·963	10·86	·04983	1·0900	134·8
	17·99	21·19	·09868	1·1780	114·7
	19·84	23·70	·1114	1·1946	111·5
	23·93	29·69	·1416	1·2410	96·5
	27·14	34·55	·1677	1·2728	86·42
	29·49	38·33	·1882	1·2990	74·00
	31·86	42·14	·2104	1·3284	65·32
	38·37	53·31	·2802	1·3891	43·87
	38·90	54·31	·2865	1·3960	40·69
	42·67	61·10	·3348	1·4320	31·70
	46·05	67·36	·3841	1·4626	23·75
	47·57	70·42	·4084	1·4795	21·61
	53·13	81·06	·5100	1·5260	14·15
	56·19	87·00	·5772	1·5480	11·52
	60·95	93·38	·7025	1·5680	9·76
	64·71	103·60	·8252	1·6010	6·32
70·04	0	0	0	·97781	234·3
	13·60	15·33	0·07086	1·1269	193·0
	21·13	25·52	·1206	1·2076	162·4
	26·93	34·19	·1658	1·2683	131·7
	33·33	44·29	·2249	1·3289	101·6
	39·77	55·42	·2971	1·3937	66·82
	44·52	64·01	·3612	1·4380	46·76
	52·54	79·41	·4982	1·5113	26·20
	62·52	99·61	·7506	1·5933	12·99
80	0	0	0	0·97183	355·1
	10·95	11·90	0·05534	1·0864	314·1
	19·90	23·51	·1118	1·1815	261·4
	26·88	33·78	·1655	1·2562	209·8
	32·64	42·96	·2151	1·3162	163·5
	37·81	51·78	·2736	1·3695	119·0
	41·66	58·59	·3213	1·4070	94·60
	46·29	67·10	·3878	1·4494	69·43
	51·36	76·81	·4751	1·4958	48·54
	52·35	78·75	·4943	1·5045	45·81
	61·93	98·31	·7319	1·5869	22·64
	66·18	107·30	·8804	1·6214	16·41

The Accuracy of the Air Bubbling Method for Alcoholic Solutions.

The air bubbling method depends essentially on the validity of two assumptions :—

    (1) That Dalton's Law of Partial Pressures is valid for the mixtures of air and solvent vapour.

    (2) That the density of solvent vapour in the conditions of the experiment is normal.

In order to test the validity of these assumptions for alcoholic solutions, the vapour pressures of absolute alcohol were determined at different temperatures, and compared with the results obtained by different methods. A table of comparison is given (Table III.) from which it can be seen that the results obtained are in fair agreement with those of other workers.   This is therefore proof that the assumptions made in the air current method are valid for alcoholic solutions, and the method can therefore be used for the accurate determination of the vapour pressures of these solutions.

TABLE III.—A Comparison of the Vapour Pressures of Ethyl Alcohol
Obtained in the Present Work with Those Obtained by Other Workers.

Temperature °C.	Vapour Pressure in mm. of Mercury.						
	Authors.	Regnault.[8]	Merriman.[9]	Schmidt.[10]	Ramsay & Young.[11]	Pieper.[12]	Price.[13]
30	78·65	78·52	78·6	78·0	78·06	78·42	78·9
40	133·7	133·69	134·9	133·8	133·42	133·84	134·95
50	221·6	219·9	222·2	220·9	219·8	220·88	224·8
60	351·5	350·21	352·7	352·1	350·21	—	352·8

Vapour Pressures of Alcoholic Solutions of Calcium Chloride.

Previous Work.—The determination of the vapour pressures of alcoholic solutions of calcium chloride over a wide range of concentrations at different temperatures had not previously been attempted.   Raoult [14] determined the diminution in vapour pressure caused by the solution of one gram molecule of various substances, including calcium chloride, in alcohol, but the most complete series was obtained by Pieper [12] using the static method.   The solution was introduced into a flask connected with an evacuated barometer column, and the pressure obtained by comparison with an adjacent barometer.   The chief difficulty encountered in the static method is that of removing all air from the solution and the vessel containing it ; Pieper, however, ignores the possibility of air being present in the solution, and this constitutes a serious source of possible error in his measurements.   It is also advisable in this method to have some stirring arrangement in the solution to ensure that a fresh surface is constantly exposed, and the lack of this might introduce error.   By raising the temperature of the thermostat containing the apparatus, the increase in vapour pressure for definite small increases of temperature was obtained.   Pieper states that these increases were not regular, but that irregular increases occurred at certain temperatures ; he endeavoured to explain this on the solvate theory as due to the splitting up of the molecular complexes of

[8] *Mem. Acad.*, **26**, 339, 1862.
[10] *Z. physik. Chem.*, **8**, 628, 1891.
[12] *Bonn*, 1917.
[14] *Compt. Rend.*, **107**, 442, 1888.

[9] *J. Chem. Soc.* (*T.*), **103**, 628, 1913.
[11] *Phil. Trans.*, **177**, I., 123, 1886.
[13] *J. Chem. Soc.* (*T.*), 1915, 188.

alcohol molecules and ions or salt molecules into smaller aggregates. This cannot be verified by the method used in the present work, but the existence of such irregularities is unlikely, as they have not been observed in such cases as calcium chloride in water, where the presence of definite hydrates is known; the curves obtained are in all cases smooth. A table of comparison of the results obtained by Pieper with those obtained in the present work is given for pure alcohol and for the only concentration investigated by Pieper :—

Alcohol.	30° C.	40° C.	50° C.
Miss Hayward & Perman	78·6	133·7	221·5 mm.
Pieper	78·42	133·84	220·88 ,,

Concentration 3·191 g. CaCl₂ per 100 c.c. solution.

	30° C.	40° C.	50° C.
Miss Hayward & Perman	77·74	132·2	219·1 mm.
Pieper	75·41	127·19	207·09 ,,

It can be seen that, while the results for alcohol are in good agreement, those for the solution are very different. The results in the present work are consistently higher than those of Pieper, and are borne out by the vapour pressures obtained for solutions of neighbouring concentrations. There must be some constant error in Pieper's measurements of the vapour pressures of solutions, such as would be caused by traces of water, or possibly an error in the estimation of the concentration.

Experimental Procedure.—The calcium chloride used in this work was Kahlbaum's "Medium Granular," which was shown by analysis to be superior to other makes, the most common impurities being iron, phosphates, and sulphates. The purity was estimated gravimetrically as 99·82 per cent., the only impurity being lime. Neuberg and Rewald [15] stated that in ethyl alcohol the solubility of lime was of the same order as that in methyl alcohol, viz., 1·125 grams per litre ; it was therefore considered that the effect of the lime on the vapour pressures of the solutions would be negligible. In the preparation of the solutions, the amount of calcium chloride required was weighed out roughly, and added quickly to the alcohol, the exact concentration being obtained later either gravimetrically or volumetrically with silver nitrate solution standardised against Kahlbaum's potassium chloride.

The method of experiment was the same as for caustic soda in alcohol. The temperatures investigated were 20°, 30°, 40°, 50° and 60° C., and the concentrations ranged from dilute solutions to near saturation at each temperature. The densities over a range of concentrations were also ascertained. The solutions were allowed to stand for days in air-tight bottles to allow the lime to settle, and the clear solution decanted off, and the densities measured as before.

The results are given in Table IV.

The curves obtained from the above results become gradually steeper with increase of concentration, and show no unusual features.

Theoretical Discussion of Results.

The results for the vapour pressures of aqueous solutions of sodium hydroxide and of alcoholic solutions of calcium chloride were employed for the calculation of the heats of dilution, and the osmotic pressures of these

TABLE IV.—Vapour Pressures and Densities of Solutions of Calcium Chloride in Alcohol.

Temperature °C.	Concentration (g./100 g.).	Concentration (g./100 c.c.).	$\frac{n}{N}$.	Density.	Vapour Pressure.
20	2·710	2·196	0·01154	0·81040	43·72
	5·222	4·335	·02283	·83014	—
	6·987	5·883	·03114	·84188	42·69
	9·532	8·224	·04367	·86270	41·84
	11·68	10·26	·05478	·87877	41·16
	13·32	11·89	·06374	·89230	40·19
	13·54	12·10	·06489	·89400	40·13
	15·95	14·58	·07866	·91395	38·94
	18·08	16·92	·09147	·93576	37·43
	19·91	18·85	·1030	·94730	36·03
30	0	0	0	0·78036	78·65
	3·207	2·584	0·01374	·80566	77·78
	6·262	5·185	·02769	·82761	77·09
	8·210	6·930	·03707	·84416	76·08
	10·75	9·292	·04992	·86430	74·61
	12·87	11·34	·06125	·88080	72·99
	15·31	13·77	·07494	·89921	71·24
	16·39	14·90	·08123	·90924	69·94
	18·79	17·48	·09590	·93026	67·43
	20·50	19·36	·1069	·94428	65·37
	21·03	19·97	·1104	·94956	64·86
40	0	0	0	0·77301	133·7
	3·514	2·803	0·01509	·79945	132·7
	4·704	3·800	·02046	·80768	131·5
	6·542	5·404	·02901	·82600	—
	10·46	8·968	·04842	·85736	126·6
	16·35	14·90	·08102	·91120	118·4
	18·80	17·46	·09539	·92840	114·7
	20·56	19·33	·1073	·94037	111·5
	25·20	24·54	·1396	·97390	103·0
	26·67	26·40	·1508	·98976	99·56
50	0	0	0	0·76300	221·6
	3·013	2·368	0·01290	·78587	220·2
	6·392	5·194	·02830	·81250	216·6
	8·995	7·489	·04098	·83254	212·7
	10·85	9·198	·05047	·84738	210·4
	13·58	11·80	·06512	·86923	205·4
	16·32	14·19	·08083	·88938	200·3
	18·37	16·68	·09324	·90833	194·0
	20·90	19·43	·1095	·92948	187·6
	23·99	22·93	·1308	·95590	177·6
	26·41	25·57	·1446	·96808	171·0
60	0	0	0	0·75407	351·5
	3·249	2·538	0·01392	·78099	348·9
	7·628	6·191	·03423	·81169	340·6
	10·18	8·496	·04697	·83447	334·4
	15·54	13·60	·07630	·87465	319·3
	15·77	13·90	·07761	·88126	—
	18·80	17·08	·09598	·90811	309·8
	19·67	17·93	·1015	·91153	305·0
	22·68	21·28	·1215	·93850	292·1
	24·71	23·70	·1360	·95880	278·2
	28·32	28·02	·1638	·98947	258·0

solutions, while the vapour pressures of solutions of sodium and sodium hydroxide in alcohol were measured with a view to determining the state of the solute in these solutions.

Heats of Dilution.

The heats of dilution were calculated in the same way as by Harrison and Perman.[7]   In the case of sodium hydroxide, the heats of dilution have been experimentally determined over a large range of concentrations and temperatures by Payn and Perman,[16] while those of calcium chloride in alcohol have been determined by Vallender and Perman (not yet published).   A comparison of the calculated and experimental results is given in Tables V. and VI. ; in the case of the calcium chloride solutions, a few results only are given, all at 40° C.   A complete table of results for these solutions will be given in a later communication.

TABLE V.—SODIUM HYDROXIDE IN WATER.

(Comparison of calculated heats of dilution with those observed by Payn and Perman.)

Concentration (g./100 g.).	Temperature (° C.).	Calculated Heat (Cals.).	Observed Heat (Cals.).
30·0	20	27·3	28·5
	30	29·2	30·4
	40	31·1	30·9
	50	33·1	31·4
	60	35·2	31·0
27·5	20	17·9	19·5
	30	19·0	20·8
	40	20·4	21·8
	50	21·7	22·5
	60	23·1	22·8
25·0	20	12·9	12·7
	30	13·0	13·6
	40	14·7	15·0
	50	15·6	15·8
	60	16·6	16·7
20·0	20	5·1	4·3
	30	5·5	5·4
	40	5·9	6·4
	50	6·3	6·9
	60	6·7	7·5

TABLE VI.—CALCIUM CHLORIDE IN ALCOHOL.

(Comparison of calculated heats of dilution with those observed by Vallender and Perman.)

Concentration (g./100 g.).	Temperature (° C.).	Calculated Heat (Cals.).	Observed Heat (Cals.).
24	40	8·32	8·5
20	40	5·81	5·7
16	40	3·25	3·52
12	40	1·77	1·87
8	40	0·85	0·83
4	40	0·21	0·26

[16] *Trans. Far. Soc.*, **25**, 599, 1929.

Osmotic Pressures.

The direct determination of the osmotic pressures of these solutions has not been effected, owing to the difficulty of obtaining suitable semi-permeable membranes.   The determination from the vapour pressures is the most important of the indirect methods ; the surface layer of the liquid acts as a semi-permeable membrane.

Porter's equation [17] cannot be applied owing to lack of sufficient data. The equation that can be applied is that derived on the assumptions that the vapour of the solvent obeys the perfect gas law, and that the solutions are perfect, *i.e.*, consist of two perfectly miscible components retaining their normal molecular weights on mixing.   In such a solution there would be no heat effect or volume change on dilution.   On these assumptions, the equation obtained is :—

$$P = \frac{RT}{V_0} \log_e \frac{p_0}{p_1}$$

which is, on expansion :—

$$P = \frac{RT}{V_0}\left(\frac{p_0 - p_1}{p_0} + \frac{1}{2}\cdot\frac{(p_0 - p_1)^2}{p_0} + \ldots\right).$$

TABLE VII.—OSMOTIC PRESSURES OF SODIUM HYDROXIDE IN WATER.

Temperature °C.	Concentration (g./100 g.).	Osmotic Pressure (Atmospheres).
30	35	1575
	30	1081
	20	448·4
	15	283·8
	10	154·9
45	35	1531
	30	1119
	20	461·0
	15	273·2
	10	153·3
60	35	1379
	30	1073
	20	468·6
	15	293·5
	10	164·0
70	35	1471
	30	1059
	20	482·7
	15	324·5
	10	182·0
80	35	1431
	30	1052
	20	492·5
	15	308·6
	10	173·0

TABLE VIII.—OSMOTIC PRESSURES OF CALCIUM CHLORIDE IN ALCOHOL.

Temperature °C.	Concentration (g./100 g.).	Osmotic Pressure (Atmospheres).
20	20	84·55
	18	66·80
	16	53·60
	14	40·98
30	22	93·44
	20	74·96
	18	60·60
	16	47·90
	14	37·20
40	24	103·60
	22	88·22
	20	74·52
	18	60·20
	16	49·96
	14	39·39
50	24	96·36
	22	81·91
	20	68·48
	18	55·88
	16	44·60
	14	33·57
60	24	96·74
	22	81·02
	20	65·82
	18	55·37
	16	45·76
	14	37·41

V_0 is the molecular volume of the solvent at the temperature T, while p_0 and p_1 are the vapour pressures of solvent and solution respectively at that temperature.

The assumptions involved in this equation are not entirely justified in the case of the solutions investigated here, and the use of this equation can therefore give only an approximate idea of the magnitude of the osmotic pressures.

Summary.

1. The vapour pressures of the following substances have been measured over a wide range of concentration by the air-bubbling method :—

  (a) Sodium hydroxide in aqueous solution at the temperatures 30°, 45°, 60°, 70° and 80° C.

  (b) Calcium chloride in alcoholic solution at the temperatures 20°, 30°, 40°, 50° and 60° C.

2. The densities of sodium hydroxide in aqueous solution, and of calcium chloride in alcoholic solution were determined for a corresponding range of concentrations at the same temperatures.

3 The heats of dilution of sodium hydroxide in water, and of calcium chloride in alcohol were determined from the vapour pressure data by means of the Kirchhoff equation, and of the modified form of this due to Porter, and were compared with the experimentally determined values of other workers. The agreement was good in both cases.

4. The osmotic pressures of sodium hydroxide in aqueous solution, and of calcium chloride in alcoholic solution were calculated by the use of the perfect gas law.

THE STUDY OF CHEMICAL REACTIONS FROM POTENTIAL ENERGY DIAGRAMS.

By Axel R. Olson * (*Fellow of the John Simon Guggenheim Memorial Foundation*).

Of the many reactions which have been studied photochemically, those involving cis-trans isomerism are of special interest, for such reactions furnish the simplest examples of molecular rearrangement. The best known of these reactions is that of maleic and fumaric acids, which was studied by Warburg.[1] This reaction has been discussed so extensively in the literature that it is not necessary to do so here. A more recent example is that of di-chloroethylene which was studied by Bonino and Brüll.[2] The Raman spectra of the *cis* and *trans* forms of this compound showed that the trans compound was converted into the cis form by light. If we regard these systems as molecule + photon → molecule[1] + photon[1] we see that they are very similar indeed to the systems which Franck[3] and Condon[4] considered in their work on the intensity relations in band spectra.

* Contribution from the Chemical Laboratory of the University of California.

[1] E. Warburg, *Berliner Akad. Ber.*, **50**, 964, 1919.

[2] Bonino and Brüll, *Z. Physik*, **58**, 194, 1929.

[3] J. Franck, *Trans. Far. Soc.*, **21**, 536, 1925.

[4] E. Condon, *Physical Rev.*, **28**, 1192, 1926.

We shall, therefore, make use of potential energy diagrams to study the reactions of such systems as mentioned above, but to do so it will be necessary to idealise the molecule and to introduce simplifying assumptions which appear to be qualitatively correct.

The conventional picture of an ethylene molecule is that of two tetrahedra joined along an edge, the four other corners being joined to hydrogen atoms. This will be designated in the usual way by

$$\begin{array}{c} \text{H}\text{---}\text{C}\text{---}\text{H} \\ \| \\ \text{H}\text{---}\text{C}\text{---}\text{H} \end{array}$$
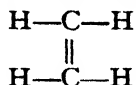
For simplicity let us assume that the lower half of the molecule is fixed in

FIG. 1.

the plane of the paper, and consider the work that is required to rotate the upper half of the molecule about the double bond. The stability of *cis* and *trans* compounds at ordinary temperatures, and the identity of the two forms in this special case lead us to postulate the potential curve shown in Fig. 1.
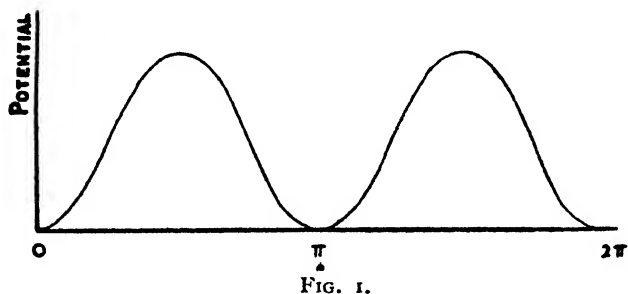
If now the two *cis* hydrogens are replaced by two groups which repel each other, these groups will furnish work which will lower the potential minimum at π as shown in Fig. 2. The difference in the two minima is approximately equal to the ordinary heat of transition. The line AA' represents the vibration of a *trans* molecule about the equilibrium position. At some higher temperature, it would change to some higher vibrational state and move along some line like BB'. A *cis* molecule would be restricted to some line like CC'.
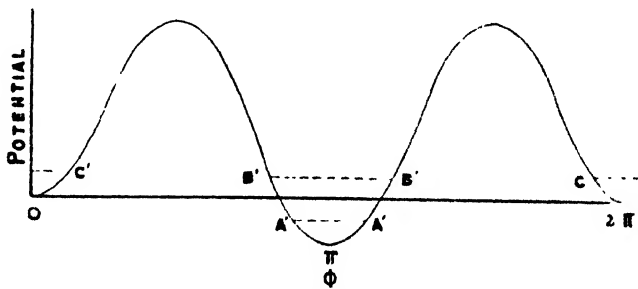
The problem of the double bond has been investigated by Hückel[5] using quantum mecha-

FIG. 2.

nical methods. His conclusions respecting the unexcited state agree very well with the chemist's conception of this state. For the excited state, *i.e.*, when the molecule absorbs a high frequency photon, we will assume at first that the potential due to the bond has cylindrical symmetry about the CC axis, and so in the upper state, since there will be no restoring force due to the double bond, only that potential remains which is due to the forces between the groups.

[5] E. Hückel, *Z. Physik*, **60**, 423, 1930.

We are now in a position to show diagrammatically the processes which occur in a photochemical reaction of this type.

The Effect of Temperature.—In order to be brief and clear, we shall neglect thermal distribution of energies among molecules, and consider only an average energy. A given vibrational state then corresponds to a definite temperature and *vice versa*. In Fig. 3 AA is the path of a *trans* molecule at some temperature *t*. When such a molecule absorbs a photon, its locus is shifted to A'A'. Since the minima of the two curves occur at the same angle, and since the curves are symmetrical about this point, the amplitude of vibration has not been changed. On the other hand the upper curve is not so steep as the lower curve and so the energy of vibration is less in the excited state than in the unexcited state. Such a molecule may :—

(*a*) return to the ground state with the emission of a photon of the exciting frequency (Tyndall light),

(*b*) return to the ground state with the emission of a photon of modified frequency (Raman lines),

(*c*) give up energy to other molecules on collision and return to the lower state (collisions of the second kind),

(*d*) acquire additional energy of vibration in collision with other molecules (represented by the line a''a'').

The possibility (*d*) is due to the fact that the vibrational energy of such a molecule is less than that corresponding to thermal equilibrium as mentioned above. From A''A'' the molecule may return to the ground state by path (*b*) or (*c*). *It does not have sufficient amplitude to return to the cis form.*
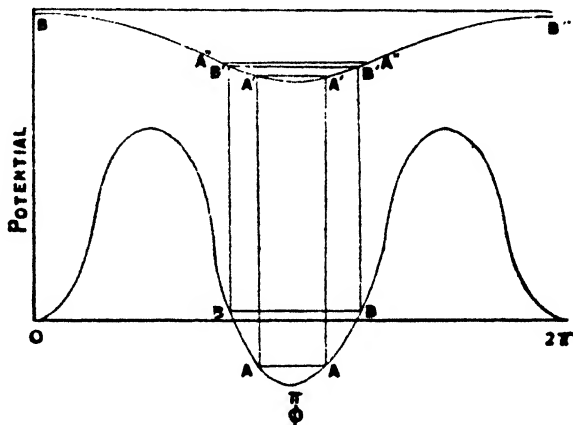
FIG. 3.

Now consider the same molecule at some higher temperature BB. On light absorption its locus is changed to B'B'. The four possibilities (*a*), (*b*), (*c*) and (*d*) must be considered as before. Of these (*d*) alone furnishes something different. Due to the higher temperature the molecule can now execute complete rotations, but the velocity of the particle will not be constant. In regions of high potential energy the velocity will be small, and so *the molecule will be in the cis state most of the time.* If the probability of the return of the molecule to its ground state by photon emission is independent of the angle between the two halves of the molecule, illumination at the temperature *b* will favour the reaction *trans → cis*.

At some still higher temperature, the upper half of the molecule will be rotating so fast that the change of potential will make only a small change in the velocity, and so we should obtain equimolar mixtures at sufficiently high temperatures.

We can summarise the effect of temperature on such a photochemical reaction by the diagram in Fig. 4.

The Effect of Pressure.—Low pressures should favour processes (*a*)

and (*b*). High pressures will favour (*c*) or (*d*) depending upon the nature of the molecules. If the pressure is due to inert molecules the establishment of thermal equilibrium will be the predominant effect and so (*d*) will be increased. If it is due to molecules which damp the fluorescence markedly, then (*c*) should be the major effect.

The Effect of Solvents.—Solvents should exert an effect wholly distinct from the effects discussed under pressure, due to their dielectric properties. We exclude of course reactions with the substance. Solvents with high dielectric constants lower the potentials, and so in general the substitution of a solvent of high dielectic properties for one of low, corresponds in some respects to an increase of temperature.
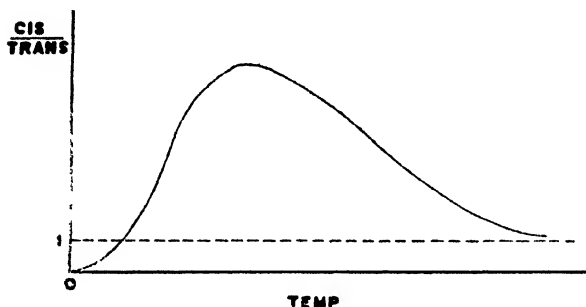
FIG. 4.

The Effect of Light Frequency.—A small change in the frequency of the incident light may of course modify the probability of absorption and also the vibrational quantum number o the excited molecule. We wish here however to restrict the discussion to such changes in the frequency of the incident light as may cause excitation to new electronic levels. At low pressures we would expect to observe changes in the fluorescent light due to the introduction of new electronic levels but not much change in the final *cis/trans* ratio. At high pressures, however, we would observe such a change. Thus in Fig. 5 consider molecules in the ground state GG. On excitation by light *vh*, they are changed into the state A'A'. For ease of discussion, assume that 10 per cent. acquire thermal equilibrium without deactivation
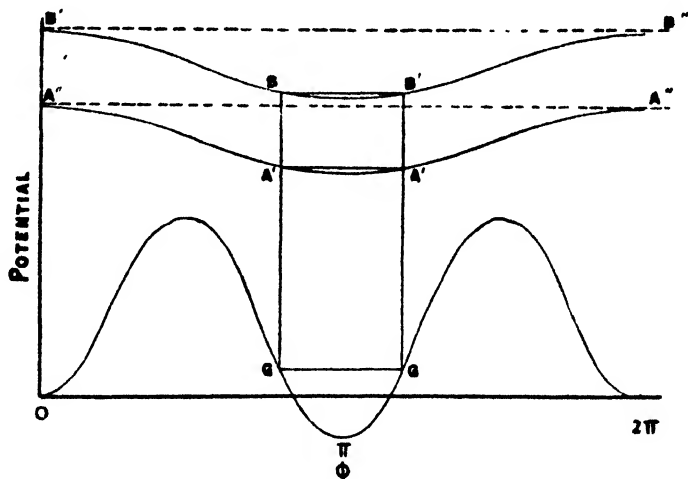
FIG. 5.

(process *d*). Of these perhaps 90 per cent. become *cis* molecules on deactivation. Thus the yield is 9 per cent. Now increase the frequency of the light to *v'* so that on excitation the molecules go into the state B'B'. As before about 9 per cent. become *cis* molecules from the state B"B", but of the 90 per cent. which do not reach thermal equilibrium in the B level, a large fraction may drop to the A level, and many of these will have acquired thermal equilibrium (process *c*), and so be represented not by

A'A', but by A"A". Thus if 50 per cent. follow this path, the total yield of *cis* will be over 50 per cent.

The simple molecular model which we have assumed permits us to calculate the allowed energy levels in the excited state and the probability that the X groups will make a given angle with each other, provided we know the forces. Since we do not know these forces, we shall assume a potential which appears to be reasonable and lends itself to easy calculation,

i.e., $V = k\, 2\, a\, \sin^2\left(\dfrac{\phi}{2}\right)$. Keeping the molecule as before in the plane of the paper, then A, B (Fig. 6) are the projections of the X groups on a plane perpendicular to the carbon bond. As one-half of the molecule turns through an angle ϕ to some new position C,

Fig. 6.

the potential function assumed above makes the work of turning proportional to BD, where a is the radius OB. Substituting this into the wave equation for a rotator we get [6]
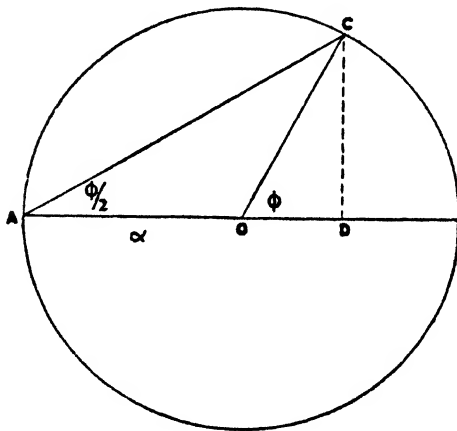
$$\frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 I}{h^2}\left[E - 2k\alpha \sin^2\left(\frac{\phi}{2}\right)\right]\psi = 0 \qquad . \qquad . \quad (1)$$

By changing to the cosine of ϕ and setting

$$a = \frac{8\pi^2 I}{h^2}(E - \alpha k) \text{ and } \theta = -\frac{8\pi^2 I}{h^2}\alpha k$$

we obtain

$$\frac{\partial^2 \psi}{\partial \phi^2} + (a - \theta \cos \phi)\psi = 0 \quad . \qquad . \qquad . \quad (2)$$

This is the Mathieu equation which has been extensively investigated.[7] When $\theta = 0$ we have the energy levels of the ordinary rotator in a plane. When $\theta \neq 0$ each level except the first splits into two, one due to an odd solution and one due to an even solution. The following table lists these a values for $\theta = -100$ which come from the first seven rotational terms.

	0	1	2	3	4	5	6
odd		− 170	− 132	− 94	− 57·5	− 22	+ 11·8
even	− 176	− 141	− 106	− 71	− 37·5	− 4	+ 27·1

Fig. 7 shows how some of these levels vary with θ.

It will be noticed that the separation of these levels does not change uniformly with θ, and so if we can identify these levels in absorption or emission spectra we may be able to determine heats of transition when moments of inertia are known or *vice versa.*

The highest energy level calculated has a value $+ 2\cdot25$ at $\theta = - 20$,

[6] In this connection see Condon, *Physical Rev.,* **31**, 891, 1928, and Pauling, *Physical Rev.,* **36**, 430, 1930.
[7] See Goldstein, *Trans. Cambridge Phil. Soc.,* **23**, 303, 1927

and so the molecule in this state makes complete revolutions. The ψ function corresponding to these conditions is shown in Fig. 8 in the graph below. The probability that the two groups shall make an angle ϕ with each other corresponds to $(\psi)^2$ and this is plotted in Fig. 9.
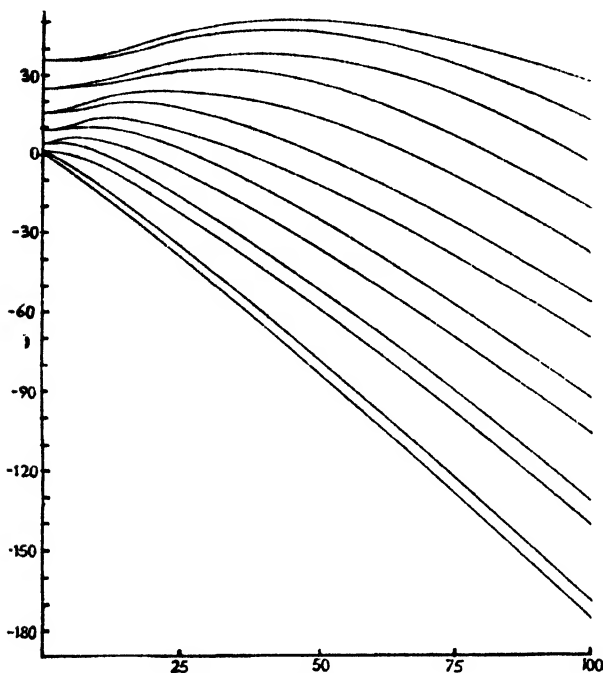
FIG. 7.

The ratio of the area under the curve in Fig. 9 lying between $\pi/2$ and π to that lying between o and $\pi/2$ is about 22. Therefore, if we assume that the electronic ψ function is independent of the rotational ψ function, we should get mostly cis form under these conditions.

The constant θ involves the product of the heat of transition and the moment of inertia. Hence an increase in the mass of the X groups, or a greater separation between X and C, or an increased force between the X groups produces a smaller amplitude of vibration at a given temperature, and therefore a decrease in the yield.

In the preceding discussion, we have limited ourselves to those systems which displayed pure vibration or rotation about the C = C axis coupled
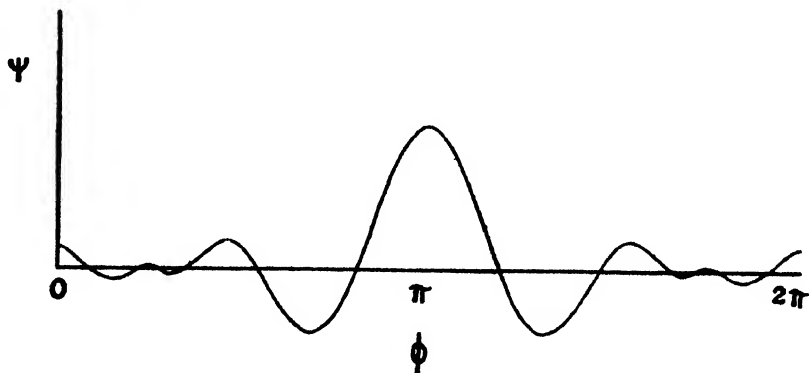
FIG. 8.

with the added restriction that the minimum in the excited states should occur at the same angle as the minimum in the ground state. If we remove this latter restriction, then the vibrational amplitude will change on excitation. Thus in Fig. 10, let AA′ represent a molecule which

absorbs a photon.   It will then be in BB' or CC', depending upon which side of the equilibrium it was at the instant of excitation.   If it emits a photon at C' it becomes a normal *cis* molecule.   Under these conditions it is possible for the reaction *trans/cis* to occur at low pressures.   At high pressures the step C'D may be due to collisions of the second kind.
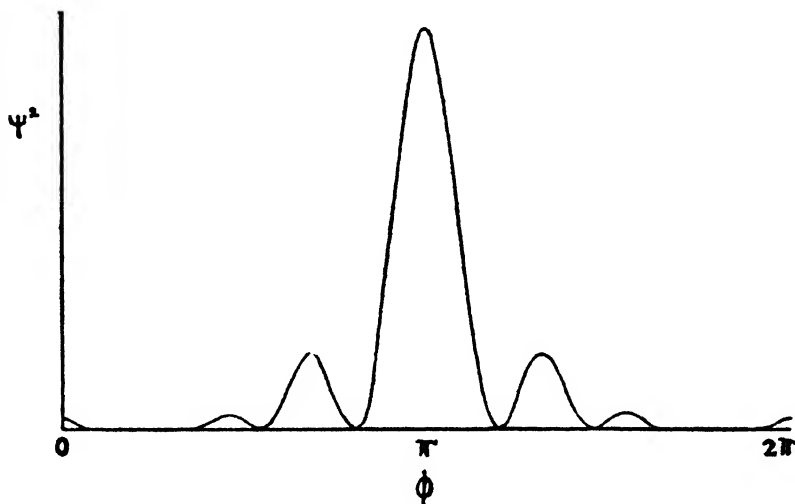
F:o. 9.

We proceed now to consider reactions which may result from a removal of the first condition, *i.e.*, rotation about the line through the centres of the two carbon atoms.   Employing the customary tetrahedra we can picture it as in Fig. 11 where the upper tetrahedron is swinging into or out

from the plane of the paper about the common corner. But such a vibration alone cannot produce a *cis* compound from a *trans* compound. To do this we must displace the upper half of the molecule in the plane of the paper so that when it has turned through 180°, the two tetrahedra again have an edge in common. The reverse of this process would be a vibration in the plane of the paper which we have called a displacement, followed by a rotation into and out of the paper.[8]
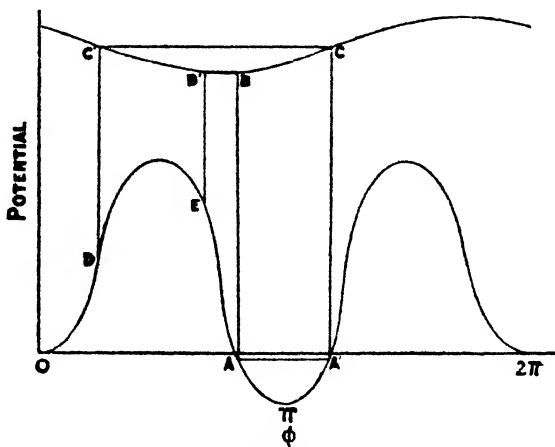
FIG. 10.

A characteristic potential energy function would be associated with each of these motions.   If the function were known the allowed energy

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[8] To preserve angular momentum such a displacement would be accompanied by rotations about an axis perpendicular to the plane of the paper.

values could be calculated and then the amplitude of oscillation about the equilibrium position for each energy level.

We have not discussed all the degrees of freedom of the C = C bond, nor have we been concerned with more complicated potential functions for the possible motion which we have discussed. Such departures from the simple functions doubtless do occur even for the simplest molecules. However, it is the purpose of this paper to emphasise the fruitfulness of a method of attack on chemical problems rather than to explore the details. Therefore, instead of pursuing these speculations further, let us see what will happen if the double bond in a *cis* compound is saturated. Obviously, if the molecule rotates about the common corner and the points YY become saturated with the same substance, the upper half of the molecule will be the mirror image of the lower half, and so an inactive compound would result. On the other hand, if the molecule executes vibration in the plane of the paper, so that opposite corners become saturated with identical substances each molecule will be optically active. However, since saturation will occur just as frequently when the upper half is displaced to the right as it will when it is displaced to the left, we would get a racemic mixture.
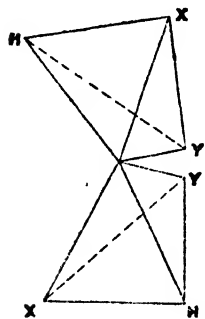
The conversion of maleic acid into tartaric acid furnishes us with an example of these two processes. In this case the direct oxidation of maleic acid by alkaline permanganate yields a mesotartaric acid, but the bromination of maleic acid with a subsequent treatment by alcoholic potash gives a racemic mixture. Differences in the dielectric properties of the solvents used and in the polarising abilities of the reagents may account for the accentuation of one type of motion over that of the other.

FIG. 11.

The specific discussions in this paper should serve to emphasise the fact that the problems of the chemist and those of the physicist are essentially the same, even though the words used to describe them differ. Heats of transition become identified with potential energy differences, rates of reaction with probabilities of transition and intensities of spectral lines, the effects of catalysts and of solvents with perturbation of the energy curves, steric hindrance with moments of inertia and potential energies, etc. True, the systems with which the chemist deals are almost always very complicated, and so simplifying assumptions must be made until sufficient experimental data accumulates to indicate how these assumptions must be modified.

In conclusion the author wishes to thank those members of the Universities of Leipzig, Bristol, and California with whom he has had the privilege of discussing various phases of this problem during the past year.

THE VIBRATIONAL LEVELS OF THE ICl MOLECULE.

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The present situation with regard to the spectrum of ICl is briefly as follows. The absorption band system in the visible region, which is mainly attributable to the more abundant isotopic constituent ICl_{35}, has been analysed so far as its vibration structure is concerned,[1] and part of the weaker ICl_{37} system has also been identified.[2] Portions of three v' progressions have been observed, the first and longest (referred to here as I) running to a convergence limit near λ 5736 Å., and the second (II) and third (III) displaced with reference to this some 380 and 760 cm.$^{-1}$ to the red. In the absence of evidence to the contrary, it would be natural to attribute progression I to absorption by molecules in the lowest vibrational state $v'' = 0$ (*i.e.* effective quantum number $= \frac{1}{2}$). But Gibson and Ramsperger concluded from observations of the effect of temperature on progressions I and II that this is not the case, but that $v'' = 1$ for progression I. This would imply that molecules in the lowest vibrational state do not give rise to bands at all, but to continuous absorption, that is to say that excitation results in dissociation instead of raising the molecule to another quantised energy level. A similar conclusion, also derived from temperature effects, had been reached by Kuhn[3] in the case of Cl_2 (but see later).

Gibson and Ramsperger also made a determination, based on the isotope effect, of the true quantum numeration (v') of the excited states of the ICl molecule, and their results were subsequently confirmed by Patkowski and Curtis, using better data and a slightly different method, which was also capable of giving the true values of v''. They found that $v'' = 0$ for progression I, in disagreement with Gibson and Ramsperger's conclusion mentioned above. No reason for the discrepancy could be assigned, and it therefore seemed desirable that their observations should be repeated with such improvements of their method as could be effected. The most obvious of these was to employ a much longer absorption tube, so that sufficient absorption could be obtained at atmospheric temperature. In their case, the tube being only 10 cm. long, it was necessary to raise its temperature to 77° C. Since their higher temperature could not exceed 200° C. on account of dissociation of the ICl, this involved a rather serious restriction of the range of temperature available. We have therefore used a tube 240 cm. long, which gives about 50 per cent. absorption at atmospheric temperature in the region of the spectrum which we have investigated. We have also employed a self-registering micro-photometer for

[1] Gibson and Ramsperger, *Physical Rev.*, **30**, 598, 1927; Wilson, *Physical Rev.*, **32**, 611, 1928.
[2] Gibson, *Z. Phy. k*, **50**, 692, 1928; Patkowski and Curtis, *Trans. Faraday Soc.*, **25**, 725, 1929.
[3] *Z. Physik*, **39**, 77, 1926.

the intensity measurements and have introduced certain other improvements into the method which are discussed in the following section.

Effect of Temperature on the Distribution of Intensity in Vibrational Progressions.

Since the distribution of the unexcited molecules amongst the v'' vibrational levels is a function of temperature, the intensities of the v' progressions originating in each of these levels will also be a function of temperature, and we may assume that the total intensity of such a progression will be a measure of the number of molecules occupying the corresponding v'' level. It is not practicable to measure this total intensity, but since there is no reason to suppose that the distribution of intensity in a progression varies with v', we may assume that the temperature variation of intensity of a particular band (v', v'') represents the variation in the number of molecules occupying the v'' level at various temperatures. That is to say, that although one cannot from spectroscopic observations deduce the relative abundance of the v'' states, one should be able to determine for any particular v'' state how the number of molecules in it is affected by temperature. For this purpose it is necessary to determine how the absorption coefficient for a particular band varies with the temperature. In practice, however, this may be difficult or even impossible, since it necessitates the use of a spectrograph capable not only of resolving the rotation structure but of showing the real breadth of individual lines. Naturally also it is necessary that the structure of the spectrum shall have been completely analysed in the region under investigation. If these conditions are not fulfilled, as in the present case, and intensity measurements have to be made on unresolved vibration heads it is not possible to determine absorption coefficients, since the law of transmission $I = I_0 e^{-at}$ cannot be applied owing to the highly selective character of the absorption. The only possibility seems to be to modify the method in such a manner as to make it depend upon the recognition of equal absorptions at two temperatures instead of upon the determination of relative absorptions. This condition was not fulfilled by Gibson and Ramsperger's method,[2] which is also open to other criticisms which need not be detailed here. But it was the basis of Kuhn's method, which consisted in heating a column of chlorine from atmospheric temperature to about 300° C., and adjusting the density so that the intensity of the first progression remained unchanged. He found that this was secured by a reduction in density to one-fifth, which agreed with the result calculated on the supposition that this progression originated in the state $v'' = 1$ instead of $v'' = 0$. His calculation was slightly in error (see next section), the true theoretical ratio being 1 : 4·25 instead of 1 : 5, but this is not sufficient to invalidate his conclusions, which have been universally accepted up to the present. Recently, however, Birge[4] has deduced from Elliott's measurements of the isotope effect[5] that Kuhn's result is incorrect, and that the first progression must be due to the molecules which are in the lowest vibrational level ($v'' = 0$). This conclusion has now been accepted by Kuhn as the result of further experimental work.[*] It is curious that there should have been a similar discrepancy between isotope and temperature results in the only two cases in which both methods have been used. The isotope method, whilst un-

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[4] Private communication.
[5] *Roy. Soc. Proc.*, A, **123**, 629, 1929; see also *ibid.*, **127**, 638, 1930.
[*] See footnote to Elliott's second paper, p. 646.

doubtedly superior to the temperature method, is of less general application, and it is therefore very desirable that the source of error in the latter should be discovered.

In the present investigation it was at first intended to use Kuhn's method, that is to obtain equality of absorption for a particular progression at two temperatures by adjusting the density of the vapour suitably. This, however, would involve a more accurate knowledge of the relation between vapour pressure and temperature than is at present available for ICl. It was therefore decided to work at constant pressure and to utilise the change of density with temperature as the means of controlling the number of absorbing molecules present. The method, whilst more convenient than Kuhn's, is less elastic, and might not be applicable in every case, although it happens to be very well suited to the case of ICl. Reserving details for the next section, we may state the principle as follows. Solid ICl is kept in a side tube at a constant temperature lower than that in the main tube, which can be maintained at various temperatures. The pressure in the apparatus being thus constant, the density in the main tube will be approximately inversely proportional to its absolute temperature. The absorption spectrum is photographed with the main tube at atmospheric temperature, and again under the same conditions except that the main tube is at about $200°$ C. It is found by calculation that the ratio in which the population of the $v'' = 1$ state is increased by this rise of temperature is almost the exact reciprocal of the ratio in which the total number of molecules in the tube is diminished, so that the actual number of molecules in the $v'' = 1$ state should remain constant. If therefore one of the progressions is found to be unaltered in intensity by the change of temperature, it may be identified as that for which $v'' = 1$.

Distribution of Vibrational Energy in ICl.

If E is the vibrational energy corresponding to a particular state, the fraction f of molecules in that state will be $\dfrac{e^{-\frac{E}{kT}}}{\Sigma e^{-\frac{E}{kT}}}$, where the summation includes all values of E actually occurring, i.e. from the lowest vibrational state to that verging on dissociation.[6] We may write E as $E_0 + v\omega$, where E_0 is the energy of the lowest vibrational state $v = 0$ and ω may be taken as constant, since it only decreases at the rate of about $0·3$ per cent. per level, and the molecules are practically all in the first three levels. We therefore have

$$f_v = \frac{e^{-\frac{E_0 + v\omega}{kT}}}{\sum_0^\infty e^{-\frac{E_0 + v\omega}{kT}}},$$

the sum being regarded as taken to infinity, since the series converges very rapidly, i.e.

$$f_v = e^{-\frac{v\omega}{kT}}\left(1 - e^{-\frac{\omega}{kT}}\right).$$

[6] We are indebted to Professor Birge for drawing our attention to the fact that the omission of the denominator $\Sigma e^{-\frac{E}{kT}}$ led to an appreciable error in Gibson and Ramsperger's calculation, which was repeated by Patkowski and Curtis. Kuhn also neglected this factor.

Since under our working conditions the total number of molecules in the absorption tube is proportional to $1/T$, the number in state v will be $\frac{T_0}{T} \cdot f_v N_0$, where N_0 is the total number present at T_0.

The values of f_v and $f_v \cdot \frac{T_0}{T}$ for the first three progressions are tabulated below, taking ω as 382 cm.$^{-1}$ and T_0 as 15° C., at intervals of 20° C. between 80° C. and 200° C.

TABLE I.

T (°K).	f_v.			$f_v \cdot \frac{T_0}{T}$.		
	$v = 0$.	$v = 1$.	$v = 2$.	$v = 0$.	$v = 1$.	$v = 2$.
288	0·851	0·127	0·019	0·851	0·127	0·019
353	0·788	0·167	0·035	0·643	0·136	0·029
373	0·770	0·177	0·041	0·594	0·137	0·032
393	0·752	0·187	0·046	0·551	0·137	0·034
413	0·735	0·195	0·052	0·513	0·136	0·036
433	0·718	0·203	0·057	0·478	0·135	0·038
453	0·702	0·209	0·063	0·446	0·133	0·040
473	0·686	0·215	0·068	0·418	0·131	0·041

It appears that when the temperature is raised from 15° C. to 200° C., the intensity of the $v'' = 0$ progression should be about halved and that of the $v'' = 2$ progression about doubled, whilst that of the $v'' = 1$ progression should remain approximately the same. The above figures refer to the total intensities of the progressions, whereas only the intensities of individual bands can be observed. In Fig. 1 are shown the intensity changes of bands in each progression which have the same intensity at 15° C. In other words, the ordinates represent for any band of a particular progression its intensity relative to that at 15° C.
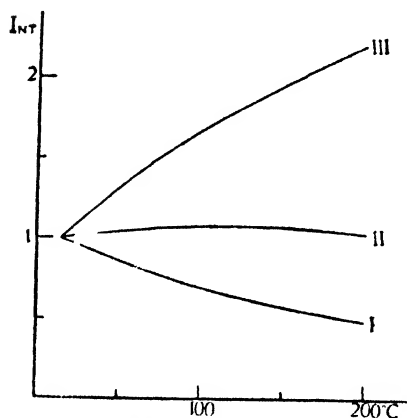
FIG. 1.—The effect of temperature on the intensities of bands which are of equal intensity at 15° C.

Experimental Procedure.

The ICl vapour was contained in a pyrex tube 240 cm. long and 2·5 cm. in diameter, having fused-on plane windows. The side tube was about 20 cm. long, bent twice at right angles and of about 5 mm. internal diameter. It was immersed in water in a Dewar flask and its temperature kept constant to within a tenth of a degree or so. The source of light was a Neron pointolite lamp of 100 c.p. somewhat under-run at about 1·90 amp. In comparison exposures the current was not allowed to vary by more than 0·01 amp., which ensured sensibly constant intensity of illumination. A lens of sufficient aperture and 5 cm. focal length gave a

roughly parallel beam along the axis of the tube. Owing to irregularities in the windows the emergent beam was not of uniform intensity transversely to the axis, and in consequence the spectrum obtained varied in intensity across its width. This would have rendered it very difficult to obtain comparable photometer records, so various devices were tried to get over the difficulty. The one eventually adopted was to interpose a sheet of ground glass between the end of the tube and the slit of the spectrograph. This gave very uniform illumination of the slit, and the loss of light, although considerable, could easily be afforded with the small dispersion used. Most of the spectrograms were taken with a Hilger constant deviation instrument, but a few were also obtained on a large Littrow two-prism instrument having a dispersion of about 8 Å. per mm. in the red. Ilford Rapid Process Panchromatic plates were mostly employed, developed with rodinal, and care was taken to find the conditions of exposure and development which would give maximum contrast.

The temperature of the tube was determined by measuring the resistance of a length of fine copper wire wound uniformly upon it. Over this was a layer of asbestos, then a uniform coil of nichrome wire, and finally several more layers of asbestos. Metal tubes, wound more closely with nichrome, and provided with glass windows, were fitted over the ends of the tube in order to prevent condensation on its windows. Before being filled with ICl the tube was highly evacuated and heated for some hours. On the first occasion the ICl was redistilled six times, the tail half being rejected each time, and finally distilled into the tube through P_2O_5, the whole operation being conducted in vacuo. The result was quite satisfactory, but when after some months' working the side tube was accidentally broken off and the apparatus refilled with the same ICl as before, considerable trouble was experienced with dissociation. This was eventually traced to insufficient drying, and it was therefore decided to leave some P_2O_5 permanently in the apparatus, between the reservoir and the main tube. This proved successful, and no I_2 bands could be detected below about 200° C. At this temperature a few came in faintly in the neighbourhood of 6100 Å., but none were visible in the region being investigated, round about 6500 Å.[7]

The procedure adopted was to make three exposures on each plate, the first with the tube at atmospheric temperature, the second with it at a high temperature, and the third after it had cooled down to atmospheric temperature again. Microphotometer records were taken of all three, and measured up. In order that these should be truly comparable, it was necessary to consider what sources of systematic error might be present. These were thought to be as follows :—

(1) Condensation on the windows. The method adopted of keeping the ends of the main tube slightly hotter than the rest, and of isolating the windows entirely from the air of the room, seemed to be quite effective. A very slight amount of condensation would have been readily observable.

(2) Alteration of the intensity of the emergent light beam due to mechanical shift, arising from the temperature change, of part of the optical system, as for instance by warping of the wooden base of the apparatus. To test for such an effect a set of blank exposures was made under the usual working conditions, except that the ICl was withdrawn

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[7] The tube appeared to improve steadily in this respect, and a few months after sealing off I_2 bands were no longer observed at 200° C. Six months after, the tube was heated to about 400° C. and still no I_2 bands were seen, although the continuous absorption mentioned later was a good deal stronger than at 200° C.

from the main tube by cooling the reservoir with liquid air. The micro-photometer records of these exposures showed that no sensible effect of this kind was present.

(3) Delay in attainment of equilibrium between the main and side tubes after changing the temperature of the former. Test exposures showed that this took place quite rapidly, but ample time—never less than an hour—was allowed between the attainment of a steady temperature and taking an exposure. Since the rate of diffusion is much decreased by the presence of a small quantity of gas in the tube, tests were made from time to time in case there might be a very slow leak in the apparatus. This was readily done by noting the time taken for the bands to disappear when the side tube was dipped in liquid air, and comparing with the result obtained directly after sealing off.

(4) Non-uniformity of illumination of the slit along its length. Although by using ground glass as described this was very slight, it could be detected with the microphotometer, and care was therefore taken that exactly corresponding parts of the three spectra were photometered. The three records were made consecutively and under precisely similar condi-tions, especially those affecting the intensity of illumination of the thermo-pile. With these precautions it was found that repetition runs gave results agreeing to within the accuracy of measurement of the trace.

It was expected that the chief source of unavoidable error would be the overlapping of progressions I and II. As explained above, the inten-tion was to find which of these was unaffected in intensity by raising the temperature. According to the evidence from the isotope effect this should be II, and a suitable section of this was accordingly selected for examina-tion. It is nowhere free from other progressions, as III begins just about where I fades out, but fortunately the heads of I lie roughly midway between those of II where the latter is strongest, so that the error due to overlapping is a minimum in this region. The heads in question are situated at $\lambda\lambda$ 6544 (II 11), 6516 (I 9), 6481 (II 12), 6449 (I 10), and 6422 (II 13), the v' numeration being that due to Patkowski and Curtis. It is evident from high dispersion (2nd order 21 ft. grating) plates of these same bands that considerable overlapping occurs, even in one progression. That is to say, the branches proceeding from one head over-run the next head, so that the latter is bound to appear stronger than it really is. This effect will be still more pronounced on heads of another progression falling between the heads of the first. We must therefore expect that if progres-sion II really remains constant, it will appear to be weakened owing to the weakening of I, and that in the same case I will apparently not decrease to the proper extent since part of the observed absorption is attributable to II. The effect of dissociation would be to weaken both owing to reduc-tion in the amount of ICl present. There is no reason to anticipate any tendency of the opposite character, namely one which would apparently strengthen either or both of the progressions.

Experimental Results.

Visual examination of the spectrum at various temperatures showed intensity changes of just the kind expected. So far as could be judged, progression II remained of constant intensity, whilst I was much weakened and III appreciably strengthened. These changes are very evident in the high dispersion photograph reproduced in the Plate, where exposures at 17° C. and 207° C. are juxtaposed. But the eye is incapable of estimating
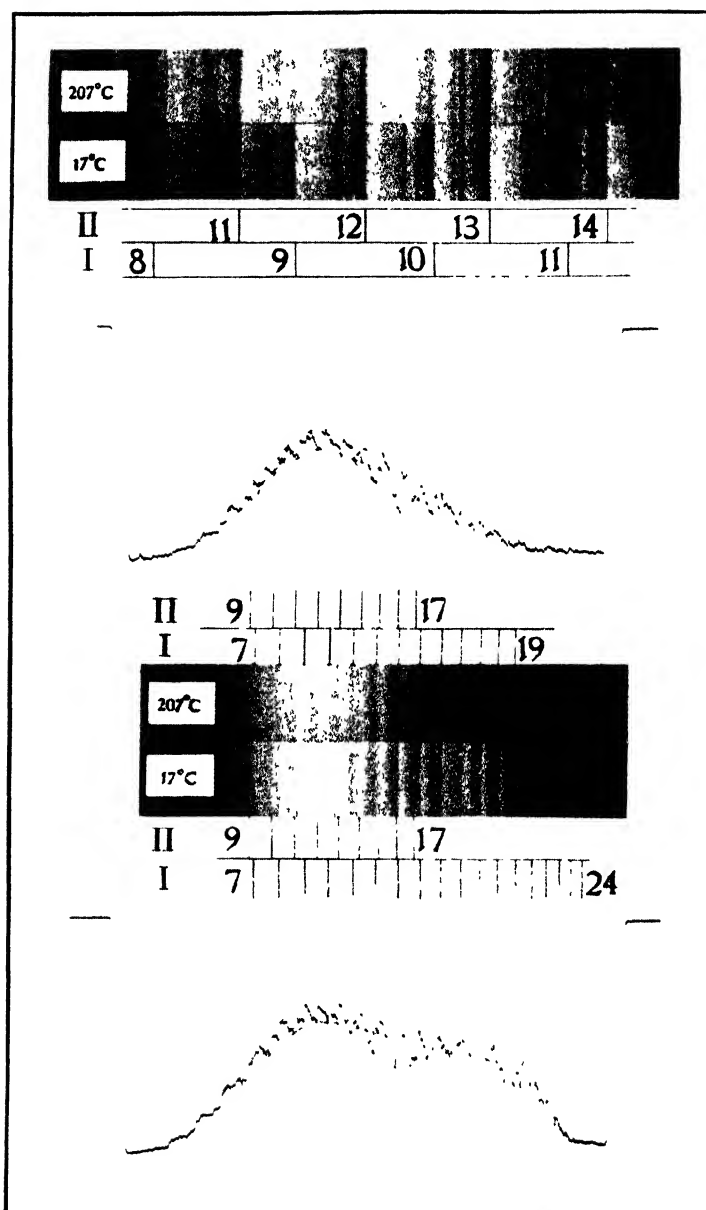
PLATE I. Temperature effect on ICl absorption spectrum.

Relative to the background curve the curve joining Prog. I head deflections is displaced upwards at 207 C from its position at 17 C whilst there is little displacement of the Prog. II curve. (Absorption increases downwards in microphotometer records.)

absolute intensities with any degree of accuracy, particularly in the case of absorption bands : visual observation gives chiefly evidence of contrast, or absorption relative to the background.   Microphotometer records of a number of the best plates showed quite clearly and consistently that the absorption increased with temperature in all three progressions.   As the measurements cannot be converted into absorption coefficients, or even into percentage absorptions, it is unnecessary to give them in detail, but as an illustration of the magnitude of the effects we may quote one set of results.   These are given in terms of the ordinates of the band heads on the photometer trace, expressed as fractions of the full scale deflection, *i.e.* that corresponding to clear negative or complete absorption, and refer to the two traces reproduced in the lower part of the Plate.[8]

	Progression I.		Progression II.		
$v' =$	9.	10.	11.	12.	13.
17° C.	·43	·44	·48	·43	·44
207° C.	·46	·48	·55	·51	·54
Increase per cent.	7·0	9·1	14·6	18·6	22·7
Average increase	8·0 per cent.		18·6 per cent.		

At first sight these results might appear to support Gibson and Ramsperger's conclusion, namely that progression I is $v'' = 1$, but such an interpretation is not tenable, since in that case this progression should have remained of constant intensity or even have decreased a little in consequence of the factors discussed in the preceding section.   There is no reasonable likelihood of its being associated with $v'' = 2$, so that there must be some disturbing influence operating which gives in this region a greater absorption at the higher temperature.

It will be seen both from the spectrograms and photometer traces that progression I extends much farther towards its convergence at 17° C. than at 207° C.   This is not due to the appearance of new bands, since the details of the structure are practically unchanged, and it must therefore be attributed to continuous absorption.   This is extremely strong towards the convergence, falling off with increasing wave-length, but in all probability it persists in sufficient strength in the region investigated to account for the effect in question.   Exposures were made at lower temperatures, from 80° C. upwards, but the difficulty could not be overcome in this way, since although this additional absorption was less, so also was the temperature effect on the bands.   Every plate taken showed the same behaviour in regard to the continuous absorption and no way of eliminating it was found. The method proposed is therefore incapable of giving the definite results which would otherwise be obtainable.

It is possible, however, to obtain some useful indications from the photometer records.   It will be noticed that at the higher temperature the whole curve is depressed, the amount of the depression increasing to the right.   Remembering that vertical distances below the zero line represent absorption, we may regard the depression of the upper envelope of the trace as measuring the increase of continuous absorption, and may obtain

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[8] Actually the traces made for measurement were much thinner than those reproduced, which were taken specially for the Plate.

a rough correction for the latter by decreasing the readings of the heads accordingly. In the small region considered this simply amounts to shifting the curve bodily upwards. If this is done it is found that the absorption for progression II remains sensibly constant, whilst that for I decreases with rise of temperature. In the case of the results given above the effect of the correction is to convert the mean increases of 8·0 per cent. and 18·6 per cent. for progressions I and II into a decrease of 9·2 per cent. and an increase of 0·7 per cent. respectively.

The above procedure is equivalent to measuring the absorption at the heads relative to the background, and we may express the result by saying that at the higher temperature the envelope of the progression II heads remains in the same position relatively to the background curve, whilst the progression I envelope approaches the latter. The three envelopes have been sketched in on the plate, in order to render the behaviour described more evident. It corresponds of course to the visual observation already recorded, that the progression II heads appeared of the same intensity at high temperatures whilst progression I was weakened. It cannot be accepted as conclusive proof of the v'' numbering (0 for I, 1 for II), but it provides strong evidence for it, since on any other hypothesis the relative constancy of II would have to be regarded as fortuitous. In the absence of any other evidence, one would undoubtedly deduce the above numbering from these observations, but not with the certainty and precision which characterise the isotope method.

FIG. 2 —Ordinates are potential energy in 10³ cm.⁻¹, abscissæ are nuclear separations in 10⁻⁸ cm.

There remains the question of the origin of the continuous absorption. Since continuous absorption must accompany each progression, it is natural to look first in this direction for an explanation. Since the continuous absorption must lie on the high frequency side of the associated convergence limit, if the former occurs in the region 6500 Å. the latter must lie above this wave-length. The lowest progression which satisfies this condition is VII ($v'' = 6$); but at 200° C. the relative abundance of this type of molecule is only about 0·07 per cent., which is far too small to give rise to the observed effect. Apart from this, there is another consideration which negatives this explanation, and which can best be explained by reference to the potential energy curves of the ICl molecule. These are shown in Fig. 2, and have been drawn by the method of Morse,[a] using the following constants: $r_0' = 2·36$, $r_0'' = 1·99$ Å.U.; $D' = 3756$, $D'' = 16,750$, $\omega_0' = 227$, $\omega_0'' = 3826$, $\omega_0'x' = 3·2$, $\omega_0''x'' = 0·6$ cm.⁻¹. The values of r_0 were not obtained directly, as the rotation structure has not yet been analysed, but were calculated from the approximate relationship given by Morse, namely $\omega_0 r_0^3 = 3000$.

In accordance with the usual interpretation of such curves, we may picture the process of absorption as a transition from a point on the lower curve representing the momentary vibrational state of the normal molecule to a point approximately vertically above on the upper curve. Since the nuclei spend most of one vibration period towards the extreme positions, the most probable transitions will be those originating near the latter. Considering first transitions from the lowest vibration state $v'' = 0$, points on the right-hand side of this level will give the bands of progression I, and points on the left the associated continuum.

Since its frequency is determined by the vertical separation of the two curves, we may predict that this should be greater for $v'' = 1$ than for $v'' = 0$, or the former continuum should lie farther to the violet than the latter. Similarly the $v'' = 2$ continuum should lie still farther to the violet, and so on for higher values of v''. There are no experimental data by which these conclusions can be tested, and the curves from which they are drawn are admittedly very approximate. They would still hold good, however, even if the potential energy functions differed considerably from those assumed, so long as they were of the same general type for the two states.

The considerations advanced seem to show conclusively that the continuous absorption in question cannot be associated with a higher progression of ICl. It cannot be due to I_2 or Cl_2 since their continua lie still farther to the violet than those of ICl. It might be due to another electronic transition in ICl, or to ICl_3, but neither explanation is free from difficulty, and the question may be left open for the present. Since the problem of ICl is a much more complex one than that of the other halogen molecules, it would probably be worth while to see whether these show any effect of this kind.

Other Characteristics of the Vibrational Levels of ICl.

It has been shown by Birge [10] that in certain molecules (notably O_2 and the halogens) the vibrational energy, and therefore also the law of force, suffers a sudden, possibly discontinuous change at a certain value of v. He reached this conclusion, undoubtedly a very significant one, by plotting $dE/d\omega$ against ω, which gave two intersecting straight lines. If the usual expression $v\omega_0 (1 - v x)$ holds good, one should obtain one straight line passing through the origin. He concludes that at this point some re-arrangement of the molecular structure occurs, but the precise nature of this is not yet known. Elliott in his second paper on Cl_2 shows that there is also a discontinuity in the course of the rotation constant B which very possibly occurs at the same point. As no results of this kind appear to have been published for ICl it seems appropriate to include them here.

The $E : \omega$ curve for the excited state was first plotted, using Wilson's data, then the slopes $dE/d\omega$ derived from this were plotted against ω. The data are not of a high order of accuracy, and the graphical determination of tangents is necessarily approximate, but it was quite evident that an abrupt change of slope occurred. The slopes $d^2E/d\omega^2$ were about 0.25 and 0.1, and the intersection was in the neighbourhood of $\omega = 101$. In order to get a more reliable value the constants in the expression $E = a + b\omega + c\omega^2$ were then obtained directly from the data by the method of least squares, separately for the two regions above and below

the discontinuity. The two parabolas represented the observations fairly well, as will be seen from Fig. 3, and the two straight lines (marked A' and B') were then directly obtained by plotting $b + 2c\omega$ against ω. The results were

from I 9 – I 18 (curve A), $a = 16734\cdot2$, $b = 9\cdot6975$, $c = -0\cdot11095$,
from I 19 – I 28 (curve B), $a = 17291\cdot2$, $b = -1\cdot5471$, $c = -0\cdot05499$.

The slopes are therefore 0·222 and 0·110 numerically and the point of intersection is at $\omega = 100$. This corresponds to $E = 16587$, this being the total energy of the molecule. The vibrational part is 2913, which is about 77 per cent. of that required to dissociate the excited molecule.

FIG. 3.—E : ω and $\dfrac{dE}{d\omega}$: ω.
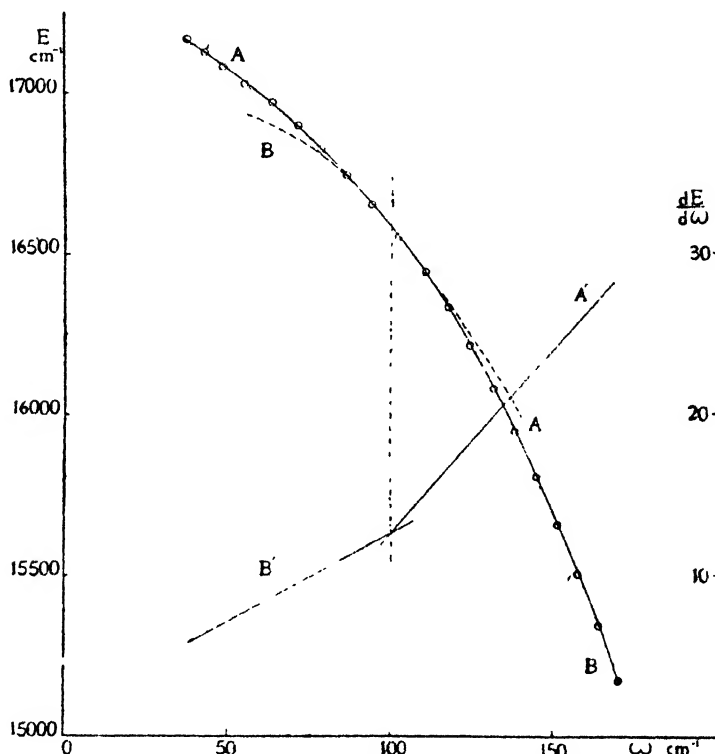
AA, BB, and A'B' are plotted from formulæ given in text.   ⊙ Observed values.

This is of quite the same order of magnitude as that found by Birge for I₂, namely 68 per cent. Elliott finds the discontinuity in Cl₂ to be in the neighbourhood of $v' = 11$, which also corresponds to 68 per cent. of the dissociation energy, but there is an uncertainty in this figure of perhaps 10 per cent.

There is one other feature of the spectrum which calls for remark, and which can be seen by reference to the Plate, namely the abnormal appearance of the band head I 16 with respect to its neighbours on either side. They are all clearly double, due to the two isotopes ICl_{35} and ICl_{37}, but the latter (i.e. the weaker) head appears to be suppressed in the case of I 16. The effect cannot be attributed to a fortuitous grouping of rotation

lınes, since the photometer records show the total absorption to be definitely less than in the other cases. It is presumably a perturbation phenomenon, but one of a distinctly unusual character.

Summary.

The effect of temperature on the relative intensities of the vibrational progressions of ICl has been investigated between atmospheric temperature and 200° C. with a view to discovering the source of a discrepancy between the results previously obtained by such measurements (Gibson and Ramsperger) and those based upon the isotope effect (Patkowskı and Curtis). Since the rotation structure was unresolved, it was not possible to determine absorption coefficients, and it was therefore necessary to use a method depending upon the recognition of equality of absorption. It was found by calculation that under the conditions of the experiment the progression $v'' = 1$ should be unchanged in intensity by raising the temperature from 15° C. to 200° C., $v'' = 0$ should decrease by about 50 per cent., and $v'' = 2$ should increase by about 100 per cent. Microphotometer records showed that all the progressions increased appreciably, but this was considered to be partly due to continuous absorption superposed on the bands which also increased with temperature. This invalidated the method proposed, and was presumably responsible for Gibson and Ramsperger's result. It could not be eliminated, but there was some evidence that apart from this the second progression would have remained constant and was therefore to be identified with $v'' = 1$. This indicates that the first and longest progression originates in the lowest vibrational state $v'' = 0$, as concluded by Patkowski and Curtis.

The cause of the continuous absorption is not known, but it is shown by consideration of the potential energy curves of the ICl molecule that it cannot be the continuum associated with some higher progression.

The vibrational data have been examined for evidence of the abrupt change in the law of force which was found at a particular value of v' for O_2 and I_2 by Birge. This occurs also in ICl near $v' = 18$, the corresponding vibrational energy being about 77 per cent. of that required for dissociation.

REVIEWS OF BOOKS.

Chemische Thermodynamik.   Einführung in die Lehre von dem chemischen Affinitäten and Gleichgewichten. By HERMANN ULICH. (Dresden and Leipzig : Verlag von Theodor Steinkopff. 1930. Pp. xvi + 353. Price : 8·50 R.M. or 20 R.M. bound.)

Dr. Ulich is known as a joint author of a comprehensive treatise on Thermodynamics which appeared last year (Schottky, Ulich and Wagner, Thermodynamik, Berlin, 1929), and the work which he did in the preparation of this treatise has made it possible for him to write a smaller and more elementary book on the same lines which is intended to serve the needs of chemists, physiologists and geologists who wish to make use of thermodynamic methods in their work. The treatment is adapted to such readers, stress being laid on clearness of exposition and close contact with numerical problems throughout. The symbols used are those of the larger treatise, and there is no doubt that in systematising the notation of the subject the author has made it difficult to fall into the pitfalls which some investigators have unfortunately not seen in using the notation of partial molar quantities. At the same time the large number of special symbols may at first sight prove rather confusing to English readers, since many of them are in German characters. There are, for example, ten different kinds of letter U, nine

of letter S and eight of letter W, and some of these are very difficult to dis-
tinguish except when they occur together on a page, since in some cases only
slight differences in size distinguish the different symbols. The three letters W
shown on the top right-hand corner of p. xiv, for example, are not at all easy to
distinguish in the text. The notation of Lewis and Randall, although less logical
perhaps, is much easier to write, print and comprehend. This is a small matter
and it is realised that the choice of a notation in chemical thermodynamics, where
so many magnitudes are involved, is a matter of great difficulty.

The activity is used freely and the methods of Lewis and Randall are generally
followed, with some differences in detail. The use of partial molar quantities and
the corresponding coefficients is carefully explained, the equations being developed
by strict methods and illustrated by well-chosen numerical examples. The
applications of the subject, in fact, take up about half the book, a feature which
will make an appeal to the type of reader for whom it is intended. The mathe-
matical equipment assumed is of a very modest order and is practically confined
to the notation of the calculus and a few simple applications. One or two more
difficult points are fully explained in foot-notes. The book is very well printed
and illustrated on excellent paper and is provided with a good index. It may be
recommended as a clear, accurate and practical account of modern thermo-
dynamics suitable for students and investigators who may have occasion to apply
that subject in their work. The very practical treatment will also make the book
useful to chemists engaged in the study of technical problems.

J. R. PARTINGTON.

Applications of Interferometry. By W. EWART WILLIAMS, M.Sc. Pp. viii
+ 104. F'scp. 8vo. [Monographs on Physical Subjects, Messrs. Methuen
& Co, London.] Price 2s. 6d.

This volume makes a special appeal to physicists. Physical chemists will be
chiefly interested in the account of the improved forms of Rayleigh refractometer.
Its accuracy is so high that even with the permanent gases the refractive indices
of which are comparatively close, a displacement of $\frac{1}{10}$ fringe with 100 cm.
chambers will occur when 0·01 per cent. of hydrogen is present as an impurity
in air A similar displacement would be given by 0·006 per cent. of Helium and
0·0095 per cent. of carbon dioxide. It is used in testing the permeability of
balloon fabrics to hydrogen and the quantitative analysis of flue gases With
shorter cells it can be used for testing the salinity of sea-water and the concentra-
tion of standard salt solutions. In the biochemical examination of blood serum
a special 1 mm. chamber has been employed. The Haber-Löwe type of inter-
ferometer is a portable type which can be strapped to the observer for the
examination of mine gases.

A rapid survey is made of a great variety of interferometers with a discussion
of the important parts of each in their application to terrestrial and celestial
questions. Mr. Williams has a practical knowledge of the subject and is himself
responsible for some of the devices that are now on the market.

As for the other volumes in the series, it should be added that the book is not
a primer but carries the subject beyond what is usually found in textbooks.

THE REDUCTION OF ARSENIC ACID AND AR-SENATES TO ARSINE AT THE MERCURY CATHODE. PART I.

By WILLIAM VERNON LLOYD, M.Sc.

The electrolytic reduction of arsenates and arsenites has been thoroughly investigated by a number of authors[1] from the analytical standpoint. In these investigations, the quantities involved in the reduction were small, fractions of a milligram of elemental arsenic; it has been shown by many workers[2] that the mercury electrode gives the best results. It has been suggested by Sand and Hackford[1] and by Harkins[3] who used the Marsh method that the efficiency of this electrode is partially due to its cathodic overpotential. Thomson[1] considered the efficiency of reduction independent of overpotential and current density. The influence of current density in the literature has been considered of no importance, and in fact has not in most cases been mentioned.

The present work was undertaken to discover the potential changes which take place at mercury and other electrodes during the reduction in acid solutions of varying concentration with respect to arsenic content, the relation between current density and reduction capacity, and the effect of the addition of metallic salts to the electrolyte upon the yield of arsine.

The majority of the solutions used contained quantities of elemental arsenic in the quinquevalent state which were much greater than have been examined before, namely from 13·8 mg. to 82·6 mg.

Experimental.

The electrolytic cell was a porous pot of 50 c.c. capacity and contained in all the experiments 40 c.c. of electrolyte. This was closed with a rubber stopper, through which passed two tubes, one to admit hydrogen when necessary and the other to carry off the products of electrolysis. In the centre of the stopper was fitted a cork, through which passed the tube which allowed the arsenic solution to pass to the cathode and also the tube carrying the mercury, as shown in Fig. 1. The cork was used so that in closing the cell, the relative position of the capillary and the surface of the mercury would remain unaltered. The mercury was held in a cup at the end of the tube. The anode was platinum gauze stretched around the pot on the outside. The pot was placed in a beaker of 50 c.c. capacity. The electrolytic gas was led from the cell through an inch of water in a test

[1] Thorpe, *J. Chem. Soc.*, **83**, 974, 1903; Sand and Hackford, *ibid.*, **85**, 1018, 1904; Thomson, *Chem. News*, **99**, 157, 1909, etc.
[2] Ramberg, *Lunds. Univ. Arrskr. N.F.*, (2) **21**, 1, 1918; Aumonier, *J.S.C.I.*, **46**, 341, 1927, etc.
[3] *J. Amer. Chem. Soc.*, **32**, 518, 1910.

tube, so as to rid the gas of acid spray and then into a U tube of neutral calcium chloride, which had been prepared by allowing crystalline calcium chloride to stand in a vacuum desiccator for two days. The quantity of arsine in the gas was determined in three ways:

(a) by passing the gas through a heated silica tube of 3 mm. bore,
(b) by passing the gas through $N/10$ iodine solution,
(c) by passing the gas into an absorption bulb containing $N/4$ silver nitrate solution.

Concordant results were obtained by these methods.

Before each experiment, pure mercury was placed in the cup and the capillary so adjusted as to just touch the surface of the mercury. The test solution containing the arsenic was placed in a small dropping funnel, which led to the mercury surface. Thus the test solution was sprayed on to the cathode for times (referred to later as the " capillary times ") which varied according to the size of the capillary (from 20 to 80 minutes). The cathode was thereby offered good facilities for reducing the arsenic solution.
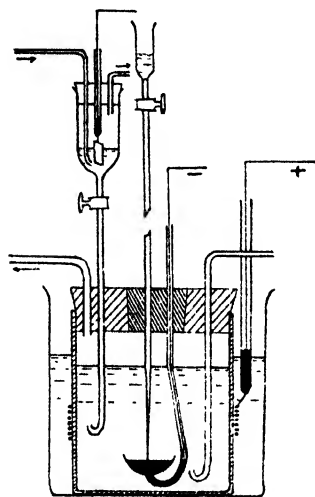
FIG. 1.

Where the commutator method was used for measuring the cathode potential, the cathode was connected alternately, 3000 times a minute, to the source of current and a potentiometer respectively by a rotatory commutator.[4] This enabled the overpotential of the electrode to be determined, measured against a hydrogen electrode working in the same solution.

In the experiments where other metals were used as cathodes, the mercury cup was replaced by a rectangular prism of the metal soldered on to a piece of copper wire, which passed through the cork. The largest face of the cathode was left exposed, the remainder and the copper wire inside the pot being coated with sealing wax. The capillary was pressed against the centre of the exposed face.

Commutator Experiments.

The object of these experiments, in which $2N$ sulphuric acid was the electrolyte and the test solutions were 10 c.c. of $2N$ sulphuric acid containing 20·8 mg. or 82·6 mg. of quinquevalent arsenic, was to determine the potential changes at the mercury cathode during the time when the reduction was taking place, measurement being made every minute.

Observations.—(1) During each experiment the commutator overpotential decreased from the value of that of mercury in $2N$ sulphuric acid, namely 0·920 V. to 0·450 V. (± 40 mV.). The rate of decrease was approximately independent of the rate at which the arsenic flowed on to the cathode. This is shown in Fig 2, which shows the relation between overpotential and time for three experiments, where the test solution was introduced in 35, 19 and 9 minutes respectively. From this it will be seen that a decrease of 0·5 V. is affected in 13, 9 and 8·5 minutes respectively.

(2) It would appear that by this method arsenic is deposited on the mercury surface in sufficient quantity to reduce the commutator over-

[4] Sand, Grant, and Lloyd, *J. Chem. Soc.*, 378, 1927.

potential to the value of that for an arsenic cathode in the same solution when arsine is being liberated.[5] The decreasing overpotential during the period when the current is interrupted apparently only permits the arsenic acid to be reduced to elemental arsenic.

(3) No arsine was produced when $2N$ sodium sulphate was used as electrolyte. This was surprising in view of the fact that the commutator overpotential of mercury in this solution was found to be very high, 1·54 V. at the commencement of the experiment and 65 mV. higher at the conclusion.

(4) Yields (calculated as weight of arsenic in the gas produced at the electrode in a given time) vary as the concentration of the test solution under the same experimental conditions.

(5) The percentage yields (i.e. the percentage of the elemental arsenic in the test solution which is produced as arsine) by the commutator method,

FIG. 2.—Overpotential in $2N H_2SO_4$, with time, test solution containing 8·26 mg. of arsenic as arsenic acid.

Curve A.—35 mins. capillary time.
   „   B.—19 mins.   „   „
   „   C.—9 mins.   „   „

i.e. with intermittent current, are small when compared with those obtained when uninterrupted current was used. The highest yield was 14·7 per cent. after electrolysis for 78 minutes in $2N$ sulphuric acid.

Experiments with Uninterrupted Current.

(a) **Cathodes of Tin, Lead, Amalgamated Tin and Amalgamated Lead.**—These electrodes have high cathodic overpotentials of approximately the same value (1·2 V.), and have the advantage that they can be easily cleaned by scraping. Test solutions containing 180 mg. of elemental arsenic were used. The following observations were made.

(1) The percentage yields were found to be small (6 per cent. at 1350 ma/cm.²), to vary with the current density and to be approximately the same for the four electrodes. There was some deposition of arsenic on the cathodes.

(2) The drop in overpotential during the experiments was smaller than in the case of the commutator experiments, e.g., for amalgamated tin a drop of 235 mV. was noted after 60 minutes electrolysis.

(3) The effect of time on percentage yield is shown in Fig. 3. That the relationship is a linear one is apparently due to there being no considerable reduction in overpotential during the reduction.

(b) **The Mercury Cup Cathode.**—In the first place, experiments were conducted where 10 c.c. of test solution containing 20·8 mg. of quinquevalent arsenic were introduced into the pot before electrolysis and also in which similar test solutions were introduced to the surface of the cathode during the electrolysis. The latter method gave larger yields (e.g., the

yields at 1260 ma./cm.^{2} were 28·8 and 46·3 per cent. respectively), and the former method was abandoned.

The relation between current density and percentage yield of arsine is shown in Table I., $2N$ sulphuric being the electrolyte, 10 c.c. of $2N$ sulphuric acid containing 20·8 mg. of arsenic acid being the test solution and the capillary time 32 minutes.

<div align="center">TABLE I.</div>

C.D. (in ma./cm.^{2}) .	70	280	560	700	840	1000	1120	1260
Percentage Yield .	5·9	15·0	22·5	27·0	33·0	33·4	34·5	32·8
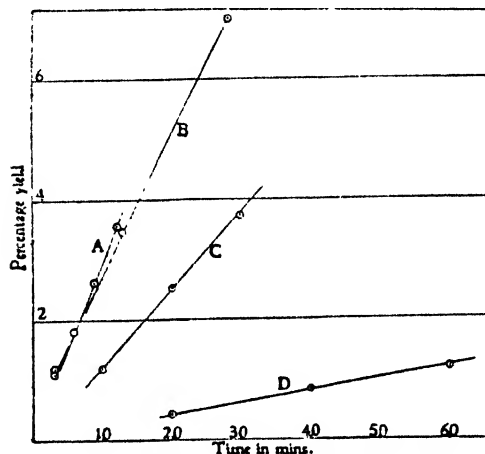
FIG. 3.—Relation between yield and time.
A.—Amalgamated lead at 1350 m.a./s.cm.
B.—   „   tin „ 1250   „
C.—   „   lead „ 810   „
D.—   „   tin „ 290   „

The yields are approximately proportional to the current density, but, at the higher current densities the heat produced during the electrolysis influences the yields.

Using $2N$ and $5N$ sulphuric acid, it was found that the latter electrolyte gave larger yields (32·2 and 48·6 per cent. respectively at 840 ma./cm.^{2}).

To show the effect of concentration of the test solutions upon the percentage yield, 10 c.c. of $5N$ sulphuric acid solutions containing 82·6, 61·9, 41·3, 20·8 and 13·8 mg. of arsenic respectively (in the proportion of 4, 3, 2, 1, 0·6 respectively) were used with a capillary time of 35 minutes at 1260 ma./cm.^{2} The results are shown in Table II.

<div align="center">TABLE II.</div>

Weight of arsenic in 10 c.c. test solution . . .	13·8 mg.	20·8 mg.	41·3 mg.	61·9 mg.	82·6 mg.
Percentage yield . . .	79·5	57·1	51·5	48·8	47·9

It is observed that with increasing dilution of the arsenic acid solution the percentage yield is greater, this being more marked in the solution containing 13·8 mg. of arsenic per 10 c.c.

The reduction in overpotential, measured by the commutator method throughout the current densities used, was the same for the same concentration of arsenic acid in the test solution. The reductions are shown in Table III., the concentrations of the test solutions being stated as mg. of elemental arsenic per 10 c.c. Initially the overpotential of the mercury was 940 mV. and the current density 840 m.a./cm.^{2}

<div align="center">TABLE III.</div>

Concentration of test solution . . .	13·8	20·8	41·3	61·9	82·6
Decrease in overpotential in millivolts	100	250	350	450	500

Besides pure sulphuric acid solutions as electrolyte, the following solutions were used: $2N$ sodium sulphate and $2N$ sulphuric acid containing $N/64$ zinc sulphate.

Using $2N$ sodium sulphate as electrolyte, no arsine was produced, although the cathodic overpotential is very high at the value of 1·525 V. This is probably due to the formation of sodium arsenate at the cathode which is apparently not reducible cathodically to arsine.

The addition of zinc sulphate to the sulphuric acid electrolyte produced larger yields of arsine. Varying concentrations of zinc sulphate ($N/4$, $N/16$ and $N/64$ were used) had the same effect upon the yield. Table IV. shows the effect of the addition of zinc sulphate on the yields using 20·8 mg. of arsenic.

TABLE IV.

Electrolyte.	Percentage Yield at 700 ma./cm.²	Percentage Yield at 840 ma./cm.²
$2N$ H$_2$SO$_4$ . . .	35·1	69·2
$2N$ H$_2$SO$_4$ + $N/64$ ZnSO$_4$	58·6	89·0

At the same time it was observed that the overpotential was initially smaller than when pure sulphuric acid solutions were used (of value 830 mV.) and that the overpotential was not only maintained during the experiment but increased by 50 mV.

In place of pure mercury, some experiments were conducted, using zinc amalgam. This was made by electrolytically depositing zinc on mercury from a zinc sulphate solution till the amalgam contained 1 per. cent. of zinc by weight. The amalgam electrode was found to be more efficient than pure mercury as shown in Table V., and also during the experiments the decrease in overpotential was small, in no case greater than 50 mV. The test solution was 10 c.c. of sulphuric acid containing 20·8 mg. of elemental arsenic.

TABLE V.

C.D. in ma./cm.²	Pure Mercury.	Zinc Amalgam.
840	32·2 per cent.	74·5 per cent.
1000	66·3 ,, ,,	87·0 ,, ,,

The efficiency of reduction, reckoned as percentage of hydrogen involved in the reduction of arsenic pentoxide to arsine during the electrolysis was calculated for all the experiments where pure acid electrolyte was used. Where zinc sulphate was used as well, the hydrogen was collected and the calculation then made. The maximum and minimum limits of the efficiencies are given in Table VI.

TABLE VI.—PERCENTAGE REDUCTION EFFICIENCIES.

Composition of 10 c.c. of Test Solution.	Minimum.	Maximum.
13·8 mg. As in $2N$ H$_2$SO$_4$	1·71 per cent.	3·89 per cent.
20·8 mg. ,, ,,	1·89 ,, ,,	7·60 ,, ,,
82·6 mg. ,, ,,	9·20 ,, ,,	14·1 ,, ,,
20·8 mg. ,, $2N$ Na$_2$SO$_4$	2·37 ,, ,,	11·12 ,, ,,

Summary and Conclusions.

Experiments have been conducted on the reduction of arsenic acid, using lead, tin, mercury, amalgamated lead and tin cathodes with a view to discover the potential changes involved and the yields of arsine produced. The test solution containing up to 180 mg. of elemental arsenic as arsenic acid has been admitted to the active cathode in periods varying from 20 to 60 minutes.

By a commutator method the overpotential has been shown to decrease by 0·5 Volt to a value representing the overpotential of arsenic, which suggests that some arsenic is deposited on the mercury cathode : analysis

of the mercury cathode showed none, and that the quantity there is small is shown by the fact that when put into a pure sulphuric acid solution, the normal cathodic overpotential of mercury is quickly established.

Using uninterrupted current, the decrease in overpotential is found to be less and varies directly with increasing concentration of the arsenic acid in the test solution. In view of this decrease, the reduction of the whole of the arsenic acid in the concentrations used to arsine presents difficulty. Where the electrolyte contained zinc sulphate, the overpotential, although initially lower than that of mercury in pure acid, was maintained and even increased during electrolysis and a bigger yield of arsine was obtained. The decrease in the overpotential of the zinc amalgam cathode was small and the yield of arsine greater.

The efficiency of cathodes for reducing arsenic acid is not dependent on the overpotential alone, lead, tin not being so efficient as pure mercury at the same apparent current densities, although the overpotentials are approximately the same. Further, using a mercury cathode in $2N$ sodium sulphate produced no arsine although the commutator overpotential was very high, -1.525 Volt. The catalytic action of the material of the cathode is also possibly an important factor.

The reduction is facilitated by increasing the current density, the strength of the acid electrolyte and the time of electrolysis. Also the quantity of arsine produced is larger the greater the concentration of the arsenic acid test solution, although the percentage yield is diminished.

The efficiency of the reduction process, reckoned as the percentage of hydrogen produced at the cathode which is converted to arsine, varied from to 1.71 per cent. to 14.1 per cent. under the best conditions.

The author wishes to express his thanks to Dr. Sand for his interest and advice during the course of this work.

Sir John Cass, Technical Institute,
London, E.C. 3.

REACTION VELOCITY IN THE SYSTEM Ag₂CO₃ ⇌ Ag₂O + CO₂.

BY WILFRED DEVONSHIRE SPENCER AND BRYAN TOPLEY.

In an earlier paper[1] measurements of the rate of decomposition of crystalline silver carbonate are interpreted in terms of a mechanism according to which the reaction takes place in the interface between the two solid phases, and the relative rates of the simultaneous forward and reverse reactions depend on the adsorption equilibrium in this interface. The detailed consideration of this mechanism led to an equation connecting the (net) rate of decomposition in the presence of carbon dioxide below the dissociation pressure, with the actual pressure or partial pressure of the carbon dioxide in the gas phase :

$$R/R_0 = (p_e - p)/(p_e + Kp)$$

[1] *J. Chem. Soc.*, **131**, 2633, 1929.

where R/R_0 is the ratio of the rate in the presence of carbon dioxide at pressure p, and in its absence; p_e is the dissociation pressure, and the coefficient K is a function of temperature. This equation, with the one arbitrary constant K, reproduces the experimental results for the range of carbon dioxide pressures up to p_e, for the three temperatures at which complete curves were obtained.

At pressures higher than the equilibrium value the reaction becomes a (net) recombination for which the equation predicts asymptotic approach to the rate $R/R_0 = 1/K$ as the carbon dioxide pressure is increased; the reaction rates measured above the equilibrium pressure do not, however, accord with this result, for the reason that the zone of reaction is no longer defined solely by the propagation of the original interface through the solid.[1] Measurements of reaction rate have now been extended to the recombination of the silver oxide with carbon dioxide, and the subsequent decomposition of the carbonate so formed. The kinetics now studied refer to the system after the well-defined crystalline nature of the original silver carbonate has already been destroyed by the initial decomposition.

The oxide formed even in the first decomposition of the crystalline carbonate must be presumed to have a complex physical structure, as also must the "synthetic" carbonate, so that the particle size and the effective surface cannot be estimated even approximately; consequently the *absolute value* of the reaction rate has no theoretical interest. The results obtained in respect of the change in the type of reaction curve when the conditions are varied do, however, throw light upon the mechanism of the reaction; moreover the general features of the kinetic behaviour of this system may well be typical of many of the type *Solid* (1) $\rightleftharpoons$ *Solid* (2) + *Gas*, so that the results have also a bearing upon the purely practical problem of absorbing a gas by chemical reaction with a solid.

The account given here is a summary of over two hundred experiments, many of which were consecutive runs carried out with the same sample of solid, simply by introducing and removing carbon dioxide. The following points have been studied: (1) the recombination of silver oxide, and the decomposition of the "synthetic" silver carbonate, in the presence of carbon dioxide at different pressures; (2) the influence of temperature upon the decomposition of the "synthetic" carbonate; (3) the behaviour of the system on successive recombination and decomposition; (4) the effect of water vapour.

Experimental Method.

The reaction was measured by weight change on a quartz spiral spring microbalance, exactly as previously described. Crystalline silver carbonate from a solution of the bicarbonate was used as the starting point, the oxide being prepared by decomposition of this material in the apparatus itself. The volume of the reaction vessel, spring balance case, manometer and leads was sufficiently large to render negligible the pressure exerted by the few milligrams of carbon dioxide produced or removed in the reaction, which therefore took place at constant pressure of carbon dioxide.

Influence of Carbon Dioxide Pressure on the Recombination.—The experiments were all done at $158°$, where the equilibrium pressure is normally [2] 75 mm. (*i.e.* for the crystalline material); but after a number of

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[2] Centnerszwer and Krustinson (Z. *physikal. Chem.*, 124, 255, 1926) recorded a similar behaviour during their determination of the dissociation pressure of silver carbonate by a dynamical method.

successive recombinations and decompositions a material is obtained which will decompose slowly at this temperature in the presence of carbon dioxide at 90 mm., though slow recombination takes place with 105 mm.; ultimately a product was obtained which had an equilibrium pressure of about 115 mm.

The sample of solid used in this series of experiments had already been decomposed and re-carbonated ninety times at a lower temperature, and had settled down to giving quite repeatable results. The carbon dioxide was not specially dried by phosphorus pentoxide.

The results are illustrated by the curves in Fig. 1. Ordinates represent
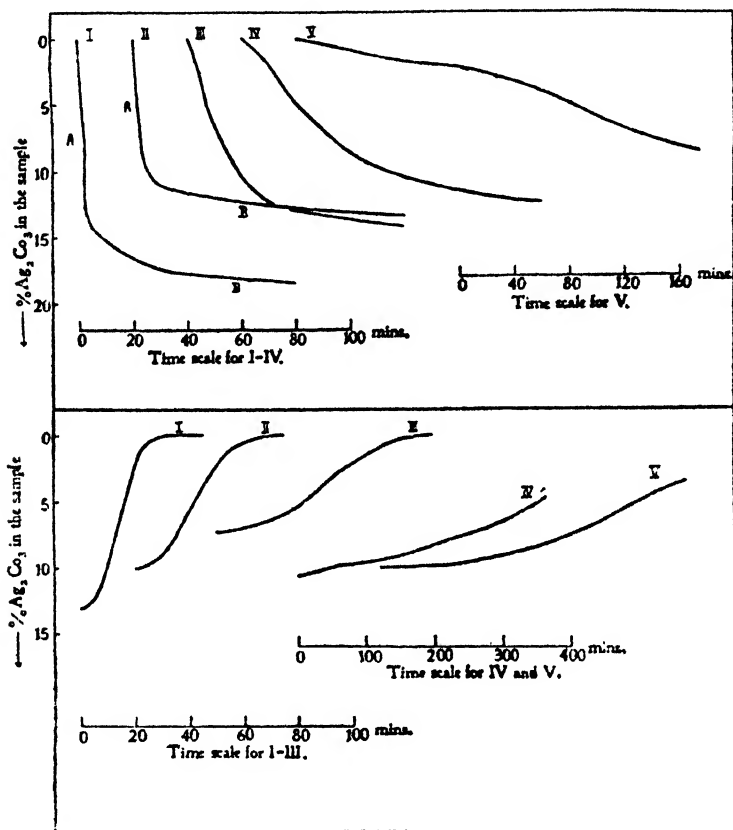
FIG. 1 (Upper).—Recombination of Ag_2O with CO_2.

I. 513 mm.   II. 475 mm.   III. 237 mm.   IV. 250 mm.   V. 145 mm.

FIG. 2 (Lower).—Effect of CO_2 on the decomposition.

I. *In vacuo*.   II. 10 mm.   III. 30 mm.   IV. 50 mm.   V. 70 mm.

the extent of recombination expressed as the percentage of complete reaction, plotted against time on a scale shown in the diagram. These curves are typical of many which have been plotted—at intermediate pressures intermediate shapes of reaction curves are obtained. When carbon dioxide at a pressure considerably in excess of the actual dissociation pressure is admitted (curve I.) there is immediate and rapid reaction (" A ") until about 12 per cent. of the oxide has been carbonated, after which the rate suddenly decreases and the reaction continues very slowly (" B "); the

" B " curve can be followed for several days, the rate finally becoming too small to measure when some 25 per cent. of carbonate has been formed.

The slow reaction " B " is discussed in another section. It is also shown later that in reactions in which the rapid and the slow parts are sharply differentiated, the *extent* of the former depends in a remarkable way upon the total extent (" A " + " B ") to which the sample was re-carbonated in the preceding recombination, in spite of the fact that in the intervening decomposition reaction the sample is brought back to the state of pure oxide. It is necessary to standardise this factor, in a series of experiments in which one parameter is varied to find its influence ; in the present series the point of interest was the change in general form of the curves with change in carbon dioxide pressure, and it was sufficient to standardise quite roughly the total extent of recombination.[3]

As the carbon dioxide pressure is decreased the initial rapid reaction becomes rather slower, and the sharp distinction between the " A " and " B " portions of the curves disappears. At the same time the curves begin to show the phenomenon of autoacceleration. (Curves III., IV., V., Fig. 1).

This behaviour provides some support for the mechanism suggested to account for the kinetics of the decomposition of the crystalline material,[1] since it receives a simple explanation on the same lines : when the pressure of carbon dioxide is only slightly greater than the actual dissociation pressure of the solid, the reaction rate is extremely slow in spite of the large surface exposed to the gas. This is the result of two circumstances. The rate of an interface reaction in a system of this type is proportional to the product of the area of the interface between the solid phases and its rate of propagation ; the equation previously found, together with the value of the constant K for $Ag.CO_3/Ag_2O$ show that the rate of propagation is very small in the neighbourhood of the equilibrium pressure. Further, if the oxide is free from carbonate the occurrence of any reaction at all is dependent upon the formation of carbonate nuclei ; now a nucleus may be assumed to have less than the full "stability" of the normal carbonate lattice and therefore a higher effective dissociation pressure, so that it is to be anticipated that a gas-phase pressure of carbon dioxide only slightly in excess of the minimum value required to hold the normal carbonate lattice in equilibrium will not suffice for the formation of nuclei. This is still true for the silver oxide-silver carbonate system which shows an enhanced dissociation pressure owing to its finely divided or complex physical condition, the normal carbonate lattice being now replaced by one having a modified average internal energy, the nucleus still having a greater tendency to decompose than the equivalent amount of carbonate definitely forming part of the modified lattice.

This is in agreement with the behaviour of the system at higher pressures. The rate first becomes large enough to measure with accuracy at about 135 mm., and the curves obtained in the region 135-235 mm. show the characteristic acceleration associated with the growth of relatively few nuclei ; the (maximum) reaction rate increases with the pressure, and at the same time the position of the maximum moves nearer to the beginning of the reaction. This is to be anticipated, since the facility with which nuclei of carbonate form will increase with the carbon dioxide pressure relatively more rapidly than the linear rate of propagation of the interface from the

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[3] Curve I. is not quite comparable with the other four, in this respect, but the difference is not important here.

nucleus as centre. At still higher pressures the acceleration disappears altogether, so that there must then be an almost immediate formation of a plentiful supply of nuclei.

The almost discontinuous form of the reaction curves at the higher pressures (curves I. and II. of Fig. 1, V.-VIII. of Fig. 3, I.-IX. of Fig. 4) show that *carbon dioxide cannot diffuse readily over the surface of the silver carbonate*. This conclusion rests upon the following interpretation : the solid oxide obtained after several recombination and decomposition reactions is considered as an aggregate of a very large number of very small particles each consisting of a fragment of oxide lattice, probably of colloidal dimensions, and in general attached at one or more points to its neighbours. (The oxide is "caked" but crumbles readily under slight pressure.) When carbon dioxide is admitted to the oxide (at 570 mm.) rapid recombination takes place until the outer layers of the sample are carbonated on the surface, to a depth of a few ionic diameters only. The reaction then slows up quite suddenly, for two reasons : (*a*) because this carbonate layer prevents any more carbon dioxide from gaining access to the interior of the individual particles, and (*b*) because the gas now diffuses only very slowly, on the carbonated surface of these particles, through the outer layers of the sample inwards to fresh oxide particles underneath. The rate of reaction during the "B" part of the curves is governed by a diffusion process. Thus a carbonate surface behaves very differently from an oxide surface, which has been shown to permit free surface diffusion of carbon dioxide.[1] It is as though (what is inherently probable) the carbon dioxide "wets" the oxide but not the carbonate surface.

According to this interpretation the very rapid recombination which finishes so abruptly is mainly a consequence of the great ease of nucleus formation with a pressure considerably in excess of the equilibrium value, together with the large area presented by the micro-crystalline oxide particles. The gain in weight measured in the first part of the reaction therefore partly—perhaps mainly—contributed by carbon dioxide combining more directly than by the ordinary mechanism involving the interface between the two solid phases.

The question of *adsorption* is discussed later, but it should be stated here that direct measurement shows that no important fraction of the weight gain is due *merely* to adsorption.

If the behaviour of this system is at all general for systems of this type, it suggests an interesting point in connection with the efficiency of gas absorption by reaction with a solid, and the conversion of one solid into another by reaction with a gas. We find that the *initial* rate of absorption is improved by increasing the ratio $P_{CO_2}/P_{equilibrium}$, but that *the total amount of reaction during an assigned time interval* (time of reaction) may be less with higher gas pressures. Comparison of curves II. and III. of Fig. 1 provides an example : the total amount of reaction after a time of reaction longer than 28 mins. is greater at 237 mm. than at 475 mm.

Consideration of the mechanism of reaction discussed in connection with the set of curves in Fig. 1 indicates that an optimum pressure, depending on the time of reaction allowed, might be expected. The condition for an optimum pressure is that :—

(1) The ratio $P_{CO_2}/P_{equilibrium}$ must not be so great that particles in the outer layers of the solid become completely carbonated on their surface through "nucleus" formation, so preventing the diffusion of the gas down to the underlying particles.

(2) The ratio $P_{CO_2}/P_{equilibrium}$ must be sufficiently in excess of unity to ensure a reasonable rate of spreading of the true interface reaction through the individual particles.

In other words, the nearer the ratio $P_{CO_2}/P_{equilibrium}$ is to unity, the greater will be the rate at which the gas reaches the underlying particles, after a definite amount of reaction has already occurred, since this rate is determined by the proportion of the surface area of the particles in the outer layers which still remains in the oxide form, upon which diffusion can occur; but on the other hand the rate of spreading of the interface reaction itself into any particle decreases rapidly as the ratio $P_{CO_2}/P_{equilibrium}$ approaches unity.

Thus the existence of an optimum pressure depends primarily upon the time interval assigned; its value is determined by a complicated balancing of the following factors :—

(1) The time interval assigned.

(2) The facility of formation of carbonate nuclei, and its variation with the gas pressure.

(3) The linear rate of propagation of the carbonate-oxide interface, and its variation with the gas pressure.

(4) The physical structure of the oxide (particle size).

(5) The speed of diffusion of carbon dioxide upon the oxide surface, for a given concentration gradient in the adsorbed layer.

Curves similar to those of Fig. 1 have been obtained at other temperatures; within the range 125° to 158° the rate over the "A" parts of the curves does not appear to change very much, but is too fast for accurate measurement with our apparatus.

Influence of the Pressure of Carbon Dioxide in the Decomposition of " Synthetic " Silver Carbonate. —The shape of the reaction curve in the absence of carbon dioxide depends upon the temperature as described later, but at 158' and above, it has the form shown in Fig 2, curve I., and Fig. 3, curves I.-IV. In the presence of carbon dioxide (Fig. 2) the rate is greatly diminished, and the reaction curves change their form, becoming more sigmoid in shape as the pressure is increased. With 10 mm. the effect is quite pronounced, and with 70 mm. the acceleration continues up to about 50 per cent. decomposition, the time required for this percentage change being 390 minutes, compared with 14 minutes in the absence of carbon dioxide. Above 90 mm. the decomposition is extremely slow. The dissociation pressure of this sample was 105 ± 5 mm. at 158°.

These results show that the spontaneous formation of nuclei of the oxide is hindered by the presence of carbon dioxide.

Other experiments have shown that if carbon dioxide is introduced into the reaction vessel after decomposition has already proceeded for some time so that an interface is already in existence, the rate is decreased qualitatively in the same way as with crystalline silver carbonate.[1]

The Influence of Temperature. —The synthetic carbonate, decomposing in a vacuum, is rather more sensitive to temperature than is the crystalline carbonate :—

Temp.	Rate.	Temp. Coefficient for 10°	
158°	·092	> 2·79	Temp. coefficient for
147°	·030		crystalline silver
136°	·0089	> 3·06	carbonate = 2·12.

In the column headed Rate are given mean values from many measurements under standardised conditions.

The temperature effect is complicated by the fact that between 158° and 136° the form of the curve changes from that associated with a ready forma-

tion of oxide nuclei, to that corresponding with comparatively few nuclei; hence the considerably higher temperature coefficient at the lower temperature is caused, at any rate in part, by a purely geometrical factor being superimposed upon the ordinary activation factor. It is clear that in this case the probability of spontaneous nucleus formation changes more rapidly with temperature than does the linear rate of propagation of the interface outwards from the nucleus as centre.

The Behaviour of the System during a Sequence of Recombination and Decomposition Reactions.—The experiments described in this section were carried out at 158°, decompositions in a vacuum, recombinations with carbon dioxide at 570 mm.—conditions such that the "A" part of the recombination curves is very rapid, and comes to an end suddenly. Fig. 3
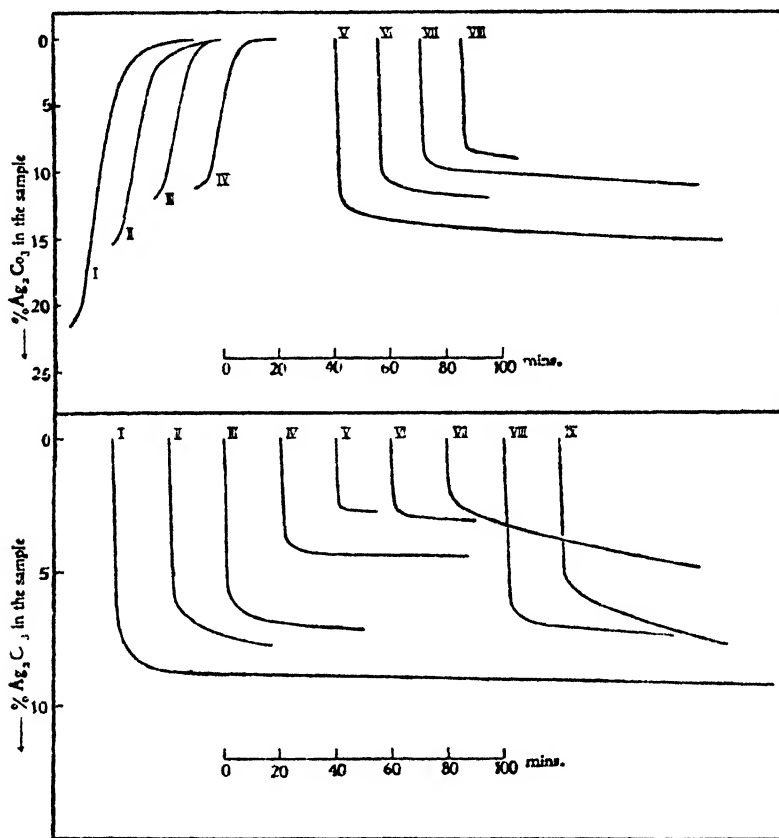
Fig. 3 (Upper).—Consecutive decomposition and recombination. reactions.
Fig. 4 (Lower).—Effect of water-vapour.

shows the curves for a few *consecutive* dissociation and recombination reactions; curve V. follows curve I., and so on. The "A" part of a recombination curve is always shorter than the preceding decomposition curve. The extent of the decomposition (which goes to completion) is, of course, equivalent to the amount of carbonate present, *i.e.*, to the total extent ("A" + "B") of the previous recombination; if, therefore, the recombination is stopped in each experiment soon after the "A" portion is completed, there is a progressive shortening of the curves. This continues until a limit is reached when only about 3 per cent. of the oxide

reacts rapidly—thereafter, if the same procedure is adhered to, there is no further change.

If, however, after this stage has been reached, the "B" part of the reaction is allowed to continue for several days, so that the decomposition curve which follows is again a long curve, then the whole series of shortening curves is obtained in the same way as before, again up to the same limit. The system will repeat this behaviour a third time, and probably a large number of times, until a slow decomposition of the oxide into metallic silver begins to interfere.

The cause of this behaviour is not very clear: the phenomenon is that a sample of silver oxide which is in a generally steady physical condition, as judged by the *reproducibility* of its kinetic behaviour, nevertheless reacts with carbon dioxide to an extent fixed by and less than the immediately preceding reaction. The decrease in extent of the rapid recombination "A" is not affected by leaving the oxide at the temperature of the experiment for 12 hours before admitting the gas. It follows that the change in the nature of the silver oxide which occurs in the course of a sequence of reactions is not a gradual one, extending over the time interval between decomposition and recombination; the change must occur either during the recombination itself, or during the preceding decomposition. The effect is not to be attributed to a progressive drying of the oxide during successive reactions, since the behaviour is the same when a small partial pressure of water vapour is kept in the reaction vessel.[4]

A possible explanation seems to be that the rapid exothermal recombination produces something analogous to sintering of the oxide particles in the region underlying the zone in which the rapid recombination actually takes place. The heat of combination is 16,300 cal./mol. The endothermic decomposition will always give rise to an unsintered oxide of loose physical structure, so that if the recombination is allowed to continue for a long time ("B"), then after decomposing the carbonate the next recombination will proceed to a greater extent before the velocity falls off abruptly.

The Effect of Water Vapour.-- In order to determine the effect of water vapour upon the recombination of silver oxide with carbon dioxide the latter was dried for three weeks over phosphorus pentoxide in a 10 l. bottle. The silver carbonate was decomposed in vacuo, with a mercury vapour pump, McLeod gauge and liquid air trap in operation. The dried gas was then admitted to a pressure of 570 mm., causing rapid reaction. The carbonate was decomposed as before, and carbon dioxide again admitted, this being repeated several times, the silver oxide presumably becoming drier each time, up to a limit, which is not, of course, equivalent to very "intensive" drying.

Drying in this way greatly diminishes the rate during the second stage of the recombination ("B"), but not much if at all during the first stage ("A"), which remains too fast for accurate measurement. After a number of repetitions of the process described above, the "B" part of the curves becomes almost horizontal. In Fig. 4 curve I. refers to the system in a very dry state; curve II. shows the effect of adding a trace of water vapour, and curves III., IV., V., and VI. illustrate the subsequent progressive drying by reaction with dry carbon dioxide and decomposition in vacuo, and also the usual shortening of the curves. The next curve (VII.) shows the effect of adding several mm. of water vapour before introducing the

⁴ The argument against attributing the effect to drying, that the whole series of curves repeats after a protracted "B" recombination, is uncertain because traces of water vapour may be evolved from the glass in the course of three or four days.

carbon dioxide : the " B " stage is now much more rapid.   Curve VIII. was obtained by continuing the evacuation for a long time after the carbonate formed in VII. had decomposed completely, so that the solid became dried out again.   Finally, curve IX. was obtained by adding a trace of water vapour again.

The conclusion which comes most clearly out of these results is that the processes which actually determine the rates in the " A " and " B " stages of the recombination must be quite different, since they differ so much in their sensitivity to adsorbed water vapour.

If the view expressed in the earlier part of this paper as to the meaning of the form of the recombination curves is correct, we must conclude that it is the surface diffusion of carbon dioxide on the silver carbonate which requires the presence of water vapour ; the reaction itself, involving the change of one lattice into the other (represented by the step $Ag_2O(CO_2)_{adsorbed} \rightarrow Ag_2CO_3$) is independent of water vapour, or requires much more intensive drying for its inhibition.

The Error due to Adsorption. —A few direct measurements have been made of the weight of gas adsorbed at different pressures.

With crystalline silver carbonate there is no measurable adsorption of either carbon dioxide or water vapour, but it must be remembered that the surface area is relatively small.

With a sample of silver oxide (about 100 mgm.) the adsorption is just measurable at the temperature of the experiments.   The sensitivity of the quartz spring was 0·01 per cent. of the weight of the silver oxide.   After correcting for the small buoyancy effect of the gas, the adsorption of carbon dioxide, expressed as a percentage of the weight of silver oxide, was 0·04 per cent. at 158° and 0·02 per cent. at 168·5°.   This refers to a saturation limit reached at about 2 mm. of carbon dioxide ; between 2 mm. and 50 mm. there was no further increase in the amount adsorbed.   Adsorption cannot, therefore, account for more than about one-tenth of the smallest amount of recombination observed in the " A " part of the curves, *i.e.*, when the limit has been reached in a sequence of shortening reaction curves.

With water vapour, adsorption on the oxide at 158° increased with the pressure up to 2·5 mm., the saturation value being 0·08 per cent. increase in weight.

Summary.

(1) Reaction rate measurements in the system $Ag_2CO_3 \rightleftharpoons Ag_2O + CO_2$ have been extended to include the recombination of the oxide with carbon dioxide, and the decomposition of the "synthetic" carbonate so formed.

(2) The type of curve obtained for the recombination depends upon the pressure of the gas and the state of dryness of the solid.   At pressures several-fold greater than the equilibrium pressure the curves are in two distinct parts.

(3) The factors determining the amount of reaction in an assigned time interval are discussed, and the possibility of an optimum pressure is accounted for.

(4) It is found that the chemically unchanged silver oxide in the region underlying the zone in which recombination has occurred is made less reactive, but that when this modified oxide is finally converted into carbonate, the oxide which it yields on subsequent decomposition is as reactive as before.

(5) Water vapour appears to promote the reaction indirectly by facilitating penetration of carbon dioxide through the carbonate formed in the first part of the reaction.   The rapid reaction in the first part of the recombination is not much affected by a degree of dryness sufficient to inhibit almost completely the second part.

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THE USE OF ANTIMONIAL LEAD FOR ACCUMULATOR GRIDS: A CAUSE OF SELF-DISCHARGE OF THE NEGATIVE PLATES.

BY J. T. CRENNELL AND A. G. MILLIGAN.

The "Aging" of Negative Plates.

In the course of an investigation of the effects of temperature and acid concentration on the performance and life of lead accumulators (unpublished work) it was observed that, particularly at high temperatures and acid concentrations, the negative plates lost capacity owing to sulphation. This was not found with new cells; but, as the cells became older, it was increasingly difficult to maintain the capacity of the negative plates. A very large excess charge was necessary in every cycle to prevent complete failure of the cells. This "aging" of the negative plates suggested either that the formation of lead sulphate by chemical reaction between the sponge lead and the acid had become more rapid, or that the charging process was less efficient in removing the lead sulphate formed in the negative plate by the normal discharge reaction.

It was therefore decided to follow the development of this condition by studying the current (or ampere hour) efficiency and other characteristics of the plates of a lead cell individually.

Method of Investigation.

The evolution of hydrogen from the negative plate on open circuit is a measure of the rate of sulphation of the sponge lead according to the reaction

$$Pb + H_2SO_4 = PbSO_4 + H_2.$$
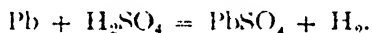
The sulphation of one mol of lead, with the evolution of one mol of hydrogen, entails the transfer of two faradays of electricity, or $53·6$ amp. hours. Hence one amp. hour of self-discharge is represented by $22·2 \times 53·6$ litres, that is 414 c.c. of hydrogen.

The gas evolved from either plate during charge is a measure of the amount of current wasted in that process; 414 c.c. of hydrogen from the negative plate, or 207 c.c. of oxygen from the positive, represent a current loss of 1 amp. hour.

A small cell was made up of one positive and one negative plate, each $8·5$ cms. by $2·0$ cms. by $0·45$ cms. The grids of both plates were of antimonial lead. These plates were fixed upside down (*i.e.* with the current-carrying lugs at the bottoms of the plates) in a rectangular glass vessel of about 700 c.c. capacity, the current being carried by pure lead wires burnt on to the lugs and led up the side of the container. The wires were enclosed in rubber tubing, so that no gas should be evolved from their surfaces. A funnel and gas-tube were fitted over each plate, so that the gas evolved could be collected and measured.

The capacity of this experimental cell was about $1·6$ amp. hours, and

was controlled, originally, by the positive plate, the capacity of the negative plate being about 2·0 amp. hours.

A second positive plate was used as an auxiliary electrode, for measurements of the plate potentials. The voltmeter used had a resistance of about 7000 ohms ; the polarisation of the auxiliary electrode when used in conjunction with this instrument was negligible.

This cell was placed in a constant temperature water-bath, and worked in cycles of charge and discharge. The single plate potentials on charge and discharge and on open circuit were observed, and the evolution of gas from the plates was measured.

The changes which gradually occurred in the behaviour of the negative plate during its life may be summarised under three heads :—

(1) The rate of gas evolution, measured on open circuit, increased during the life of the cell, at first gradually, but later more rapidly. In the new cell hydrogen was evolved on open circuit from the charged negative plate at a rate of about 0·3 c.c. per hour, in acid of density 1·220 (15° C.) and at a temperature of 25° C. The cell was worked for a year (about 70 cycles) at temperatures of 25° and 35° with acid densities 1·220 and 1·260, and combinations of these variables. At the end of the year, the rate of hydrogen evolution from the charged negative plate on open circuit was over 10 c.c. per hour in 1·220 acid at 25° C. This is an .ncrease in the rate of sulphation by a factor of over 30. A constant self-discharge of the negative plate at a rate of 240 c.c. hydrogen, or 0·58 amp. hours, per day would dissipate the normal discharge capacity of the plate in less than 4 days. The rate actually decreases with time as the available surface of the plate is reduced, and at such a low rate the available capacity is greater ; but the discharge of the plate was complete in about 7 days.

(2) The polarisation of the negative plate when gassing during charge decreased. In the new cell the difference between the open circuit potential of the negative plate and the potential when gassing at the end of charge at 0·25 amps. was 0·40 volt. After a year's working, the polarisation in the same conditions was 0·15 volt. This reduction in polarisation on charge developed in the same way as the increase in rate of sulphation described above.

(3) The current efficiency of the negative plate was very much reduced, owing to considerable wastage of current in hydrogen evolution during the whole of the charge in the deteriorated plate. In a new cell very little hydrogen evolution occurs during the greater part of the charge, and the rate increases sharply when a charge about equal to the preceding discharge has been given to the plate.

Suggested Explanation of Results.

These three observations led to the conclusion that the overvoltage necessary for hydrogen evolution at the negative plate had been reduced during the working of the cell.

The hydrogen overvoltage at any surface is controlled by the material of the surface and its physical condition—a roughened surface having a lower hydrogen overvoltage than a smooth surface.

After a consideration of various possible explanations of the observed results, it was concluded that the only satisfactory theory was that antimony from the positive antimonial-lead grid passes into solution and is then deposited either chemically or electro-chemically on the negative plate. Antimony is a more noble metal than lead, and will therefore tend to deposit on the lead surface, and to remain there in the metallic condition.

This hypothesis requires that the potential necessary for evolution of hydrogen at an antimony surface shall be less than the equilibrium potential of the lead electrode (which is itself less than the potential necessary for hydrogen evolution at a lead surface.)

If that is so, no reaction will occur when a pure lead electrode is immersed in acid; but, if antimony is deposited on the lead surface, a " local action " couple will be formed and lead will be converted to lead sulphate and hydrogen evolved from the antimony surface.

Confirmation of Theory.

(1) **Measurement of Hydrogen Overvoltage at an Antimony Surface.**—The minimum hydrogen overvoltage was measured at a surface of antimony-black electro-deposited on an antimony rod. The potential difference between the antimony cathode and a mercurous sulphate electrode, both in 7·5 N sulphuric acid, was measured on a potentiometer. The $p.d.$ between the antimony cathode and a lead anode in the same vessel was gradually increased until the first visible formation of hydrogen bubbles at the antimony surface. At this moment the $p.d.$ of the cell

$$Hg/HgSO_4 : H_2SO_4 : H_2/Sb$$
$$(7\cdot5N)$$
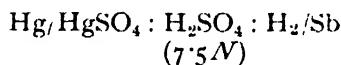
was 0·855 volt.

(The $e.m.f.$ of a hydrogen electrode against the same mercurous sulphate electrode is approximately 0·55 volt (by interpolation from Landolt-Born-stein's tables), giving a value for the hydrogen over-voltage at antimony of about 0·30 volt).

The $e.m.f$ of the cell

$$Hg/HgSO_4 : H_2SO_4 : PbSO_4, Pb$$
$$(7\cdot5N)$$
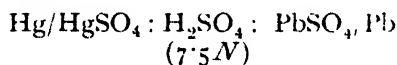
is 0·964 volt.

Hence, by difference, the $e.m.f.$ of the cell

$$Pb/PbSO_4 : H_2SO_4 : H_2/Sb$$
$$(7\cdot5N)$$
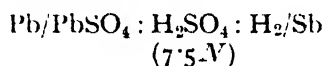
is approximately 0·11 volt.

That is to say, there is an $e.m.f.$ of 0·11 volt available for causing hydrogen evolution in the " local action " couple produced by the deposition of metallic antimony on a lead negative plate. A current will therefore flow, hydrogen will be evolved at the antimony surface and lead sulphate formed from the spongy lead.

(2) **Comparison of Cells with and without Antimony.**—Cells were made up in a similar manner to the experimental cell described above, and similar measurements made. These cells were of three kinds :—

(a) *A cell in which both positive and negative grids were made of pure lead, without antimony.*—In this cell no appreciable hydrogen evolution occurred from the negative plate when standing fully charged on open circuit, and the rate of hydrogen evolution did not increase during the life of the cell.*

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* It is an interesting fact that the rate of hydrogen evolution from the *discharged* negative plate in such a cell is definitely greater than when the plate is fully charged. The rate is about 0·25 c.c. per hour, while that in the charged cell is negligibly small (less than 0·01 c.c. per hour). This can only be interpreted as meaning that the hydrogen overvoltage at lead sulphate is slightly lower than at metallic lead.

This phenomenon should not be confused with the production of difficultly reducible

(*b*) *A cell with pure lead positive grid, but antimonial lead negative grid.*— There was a small but measurable rate of hydrogen evolution from this cell— 0·80 c.c. per hour at 35° in acid of density 1·260 (at 15°). This rate did not increase during the life of the cell, showing that the " aging " effect is not due to the presence of antimony in the negative grid. This small constant rate of hydrogen evolution must be attributed to the fact that the overvoltage at the antimonial lead grid is intermediate between that of pure lead and that of antimony (*cf.* Strasser and Gahl, below). The hydrogen overvoltage at pure lead is sufficient to prevent direct attack of the acid on the lead with evolution of hydrogen.

(*c*) *A cell with pure lead negative grid, but antimonial lead positive grid.* —The rate of hydrogen evolution in this cell was initially small—about 0·45 c.c. per hour at 35° C. in acid of density 1·270 (at 15°) — but gradually rose, and reached a value of about 4·0 c.c. per hour in the same conditions, after about 5 months, during the fourth of which the cell was standing idle. As before, the polarisation of the negative plate when gassing on charge was reduced as the cell "aged." Hydrogen evolution on open circuit and polarisation at the end of charge are plotted against number of cycles in the curves of Fig. 1.

FIG. 1.

Curve 1.—Polarisation of negative plate of cell (*c*) at end of charge at 0·3 amp.

Curve 2.—Rate of hydrogen evolution from negative plate of cell (*c*) on open circuit.

The difference in behaviour between this cell and cell (*a*) *described above, establishes the fact that an increasing rate of sulphation of the negative plate is caused by the use of antimonial lead alloy for the positive grid, and that in the absence of antimony the rate of self-discharge of the negative plate on open circuit is negligible at any stage of its life.*

Curves showing the rate of hydrogen evolution (Fig. 2) and the polarisation (Fig. 3) of the negative plate during charge have been drawn for a cell with pure lead positive grid and a cell with antimonial positive grid after 50 cycles (7 months). The effect of contamination by antimony on the behaviour of the negative plate during charge is shown very plainly.

(3) **Chemical Analysis.**— The negative plate of cell (*c*) was analysed after working for five months against a positive plate of antimonial lead.

lead sulphate in a commercial cell left standing in a discharged condition. In a commercial cell the actual rate of the reaction producing lead sulphate from lead is greater when the cell is charged than when it is discharged, for a variety of reasons—higher acid concentration, etc.

0·045 gm. of antimony was found on the surface of the plate and a further 0·040 gm. in the interior of the paste. The antimonial lead grid of the positive plate weighed approximately 31·6 gms. and contained 12 per cent. of
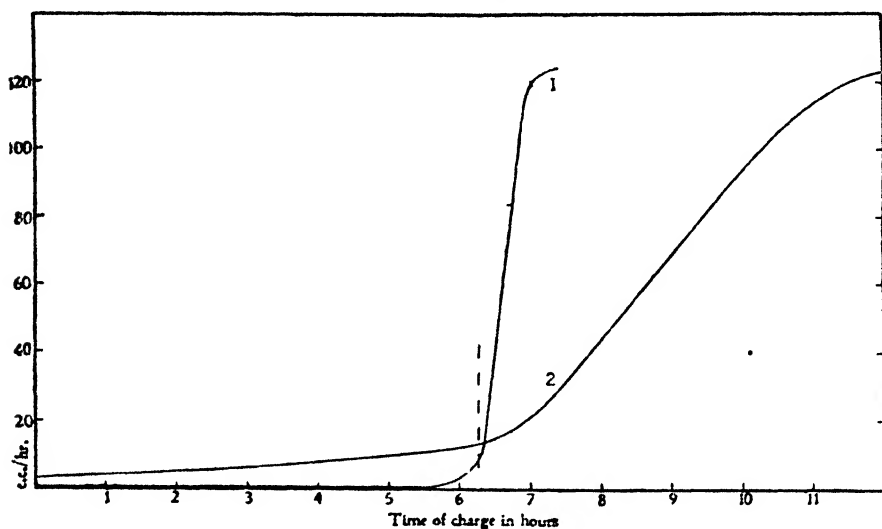

FIG. 2.—Rates of hydrogen evolution from negative plates during charge at 0·3 amp.
Curve 1.— Cell with pure lead positive grid.
  ,,   2.—Cell with antimonial lead positive grid.
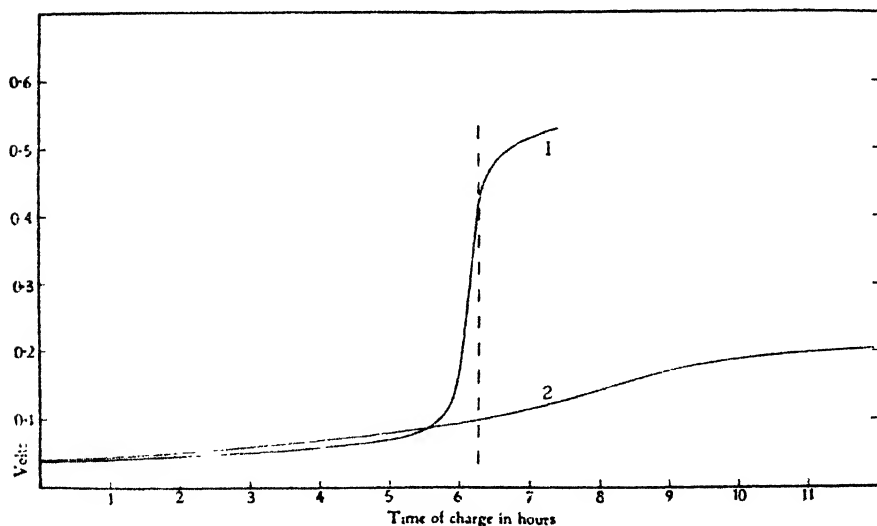(The broken line indicates where the charge equalled the previous discharge.)

FIG. 3.—Polarisation of negative plates during charge at 0·3 amp.
Curve 1.—Cell with pure lead positive grid.
  ,,   2.—Cell with antimonial lead positive grid.
(The broken line indicates where the charge equalled the previous discharge.)

antimony. The antimony found in the negative plate is, therefore, 2·3 per cent. of the total antimony in the positive grid.

(4) " **Poisoning** " **Cells by addition of Antimony.** — Antimony

added, in the form of a solution of antimony sulphate in sulphuric acid, to the electrolyte of a cell in which both grids are of pure lead produces the same effects as antimony gradually dissolved from the positive grid.

An attempt was made to obtain a quantitative relation between the total antimony added to a cell and the rate of sulphation of the negative plate. No such relation can be established, however, since in the absence of a continuous source of antimony (the positive grid) the effect of a single addition of antimony is not permanent. The rate of sulphation gradually decreases with electrical working, after addition of antimony sulphate to the electrolyte, which suggests that the antimony on the negative paste may become coated over, by repeated cycles of charge and discharge, with lead or lead sulphate, and so rendered harmless.

Antimony was also introduced into the cell by charging the lead negative plate with a rod of pure antimony as anode. Owing to the "valve" effect occurring at an antimony anode only a small current could be made to flow, but antimony slowly passed into solution, and its subsequent deposition on the negative plate produced the usual effects of increasing the rate of sulphation and reducing the polarisation on charge.

(5) **Cells of a special form** were employed on another investigation, in which the positive grid had a very much greater exposed area than in any commercial cell. These cells had positive grids of different compositions, and the negative grids in all cells were of pure lead and of the same pattern as those described above. After 50 cycles of discharge and charge (given in about 40 days), one cell of each type was dismantled for examination, and the rate of hydrogen evolution from the negative plate on open circuit was measured at 35° C. in acid of density 1·245. A second set of cells was removed after 100 cycles (given in about 70 days).

Table I. shows the rates of hydrogen evolution for negatives which had been worked against positives with grids of different compositions.

TABLE I.

	No. of Cycles.	Material of Positive Grid.			
		Pure Lead.	Lead + 2·5 Per Cent. Sb.	Lead + 7·5 Per Cent. Sb.	Lead + 10 Per Cent. Sb.
Rates of hydrogen evolution from negative plates. (c.c./hour.)	50	0·14	0·28	1·10	2·8
	100	0·15	0·48	12·7	12·8
	150	0·017	0·57	(5·0)	(14·3)

After 104 cycles new negative plates were fitted in the cells with 10 per cent. antimony positive grids, and after 114 cycles to the cells with 7·5 per cent. antimony positives, as the old negative plates were liable to reversal during the discharge.

The values for these cells after 150 cycles (which are bracketed in Table I.), therefore, refer to negatives which had only had 36 cycles in the 7·5 per cent. antimony cells and 46 cycles in the 10 per cent. antimony cells. It will be noticed that the effect of these later cycles on the gas evolution of the negatives is much greater than that of the first 50 cycles, particularly in the 10 per cent. antimony cells. This shows that the rate of removal of antimony from the positive grids is considerably higher when the grids are older.

Effect of Reversal.

Since antimony is removed from the positive plate by the ordinary charging process, it is to be expected that antimony which has been deposited on the negative plate could be removed by charging the cell in the reverse direction, making the negative plate the anode.

Experiments were made to determine whether this does in fact occur, and whether such treatment can be applied in practice to improve the condition of a negative plate in which local action due to the presence of antimony is occurring.

A small cell of the experimental type described above, with a rate of gassing of about 9 c.c. of hydrogen per hour from the fully charged negative, was charged in the reverse direction until the negative plate had had the potential of a positive for some time, and the positive plate was just rising rapidly to the potential of a negative plate. The electrolyte was then removed, and 0·092 gm. of antimony was found in it. In the normally charged cell some days previous to reversal, the electrolyte contained 0·013 gm. antimony. Antimony is therefore removed from the negative plate by reversal. The rate of gas evolution from the fully charged negative plate after reversal and recharge was about half the rate before reversal. This improvement was only temporary, and after a few cycles the original rate of local action was again reached.

If the reverse charge is continued in an attempt to remove the antimony completely, deposition of antimony on the reversed positive plate occurs. After a second (prolonged) reversal of the same cell, the positive plate, now charged as a negative, evolved hydrogen at the rate of 30 c.c. per hour, showing that antimony had deposited there and was causing rapid local action. This experiment also shows that freshly deposited antimony is exceptionally active in producing self-discharge.

A commercial cell of about 20 amp. hours capacity, in which the negative plates had "aged" badly, lost 8 amp. hours charge when standing charged for four days, owing to local action at the negative plate. After a *long* reverse charge, renewal of electrolyte, and recharge, the cell lost 15 amp. hours in 4 days. This indicates that during reversal antimony was removed from the negative and deposited on the positive plate. On recharge this antimony was redeposited on the negative plate, and in its freshly deposited condition caused local action at almost double the previous rate. The same cell was again reversed, but only to the point where the positive plate began to have the negative plate potential, so that antimony should not be deposited on the (reversed) positive plate. The electrolyte was removed in this condition and the cell recharged. In 4 days the cell now lost 9·5 amp. hours, which confirms that by correct treatment the rate of local action can be reduced. This improvement, as before, was only temporary.

Before the second reversal the electrolyte of this cell contained 0·0065 gm. antimony per 100 c.c., and when removed after reversal (to the correct point) contained 0·0285 gm. per 100 c.c.

It is clear, however, that although some of the antimony which causes local action can be removed from the negative plate by reverse charging, and from the cell by stopping the reversal at the correct point and changing the electrolyte, the improvement in performance is only partial and temporary, and that the procedure is not of practical value.

Conclusions.

It is fully established by the work described above, that in a cell with positive grids made of an antimonial lead alloy, antimony is gradually removed from the positive grids and deposited on the negative plates.   This results in a lower overvoltage to hydrogen discharge at the surface of the negative paste, setting up " local action," and also reducing the current efficiency of the plate by allowing evolution of hydrogen during the whole of the charge.   The polarisation of the negative plate when gassing at the end of charge is also reduced.   As a result of the lower *e.m.f.* available, it will be more difficult to reduce any " obstinate " sulphate existing in the negative plate.

Application of Results.

These conclusions have an important bearing on accumulator practice. Antimonial lead alloy is always used for the grids of cells of the pasted or Faure type, and, as a result, an increasing rate of sulphation of the negative plates must inevitably develop.   The reasons for the adoption of antimonial lead for the positive grid are that pure lead has not suitable mechanical properties for the intricate and delicate castings required, and that antimonial lead is considered to be less liable to " formation " of lead peroxide, with resultant reduction of grid section.

It is somewhat surprising that the damaging effect of antimony deposited on the negative plate from the positive grid has not been generally appreciated, in spite of the fact that the low hydrogen overvoltage of antimony has long been recognised.

Strasser and Gahl [1] carried out experiments on the hydrogen overvoltage at lead, antimony, and antimony-lead alloy cathodes, with special reference to the bearing of this property on the lead accumulator.   They found that with various cathodes in parallel, with a common anode, in sulphuric acid of density 1·18, hydrogen was evolved most readily from pure antimony, least from lead, with alloys intermediate.   In another experiment with equal current densities they found the following differences in polarisation between cathodes of composition as shown and the pure lead cathode.

Pure lead   zero
Lead + 5 per cent. Sb   − 0·10 volts.
Lead + 24 per cent. Sb − 0·30   „
Pure antimony   − 0·31   „

These differences were almost independent of current density.

Except in large proportions, antimony had no effect on the open circuit potential.   Its effect was to facilitate the evolution of hydrogen.

The behaviour of pure and antimonial lead sponge was also investigated.   The antimonial sponge was made by charging a pure sponge lead plate against an antimony cathode, so that antimony was deposited on the sponge.   Curves are given showing that the charging potential of a cell was about 0·1 volts higher with pure than with antimonial lead sponge, while with a smooth lead cathode the voltage was about 0·25 volts higher than at the lead sponge.   The authors state that gradually, during the life of the cell, the antimony works into the paste and the charge voltage falls considerably, a fact known in accumulator practice.

All the observations of Strasser and Gahl are confirmed by the present work.   They apparently considered, however, that the negative grid is the

source from which antimony reaches the negative paste.   It has now been shown that the antimony is actually derived from the positive grid.

While appreciating that the presence of antimony lowered the charging potential of the plate and permitted hydrogen evolution more readily, these authors apparently failed to realise that this implies a lower current efficiency for the plate, and also has the effect of allowing local action to occur on open circuit.

Vinal and Schramm [2] studied the effect of antimony among other impurities and found that it produced a rapid self-discharge of the negative plates.   Vinal [3] also refers to other investigators having shown that the presence of minute traces of antimony in the active material produces serious local action.

Parr [4] refers to local action between the negative paste and the material of the support, especially when this contains antimony as an impurity. Antimonial lead is, of course, normally used for the negative grid, and it has been shown above that a small amount of local action does occur between the paste and negative antimonial lead grid.   This is, however, of minor importance.

It has thus been frequently observed that antimony, when deposited on the negative plate, causes a self-discharge.

On the other hand, it has not been appreciated, either by scientific workers, or apparently by accumulator manufacturers, that by using antimony-lead alloys for the grids of pasted positive plates, there is not only a danger, but a certainty, that the negative plates will in time become contaminated by antimony, which will cause their self-discharge and a loss of ampere-hour efficiency.

Manufacturing Practice and Working Conditions.

The alloys used commercially for the manufacture of accumulator grids contain between 5 and 12 per cent. of antimony.

The rate at which antimony is removed from the positive grid and deposited on the negative plate will depend on a number of factors.

The higher the percentage of antimony in the positive grid, the greater the exposed area of the grid, and the more electrical working the cell receives, the more rapid will be the removal of antimony from the positive grid.

When a cell has reached the condition in which the negative plates are self-discharged fairly rapidly, owing to the presence of antimony, the capacity will be reduced unless considerable excess of charge over discharge is given, and loss of charge when standing will be serious.   That is to say, both the *efficiency* and the *capacity* of the cell will be reduced.

In giving the excess charging necessary to maintain the capacity of the cell, the condition of the negative plates is further aggravated, since antimony is removed from the positive plates during charge, and the greater the amount of charge, the more antimony will be removed, further increasing the rate of self-discharge of the negative plates.

The effect of any given deposit of antimony in causing local action will be greater at high temperatures, and high acid concentrations, because the *e.m.f.* of the lead plate is raised by these factors.

It is clear as a result of this investigation that antimonial lead should not be used for the positive grids of lead accumulators.

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[2] *J. Amer. Inst. Elec. Eng.*, 128, Feb. 1925.
[3] " Storage Batteries," p. 118.   [4] *J. Inst. Elec. Eng.*, 36, 406, 1905-6.

Summary.

(1) It has been found that an "aging" occurs in the negative plates of lead accumulators.   It is increasingly difficult to prevent self-discharge and sulphation of these plates as the cell becomes older.

(2) A method of investigating the development of this defect in experimental cells is described.   The evolution of hydrogen from the plate is used as a measure of the self-discharge and of the efficiency of the plate.

(3) It has been shown that this "aging" of the negative plate is due to the solution of antimony from the alloy of the positive grid, and its deposition on the negative plate.   The low hydrogen overvoltage at an antimony surface allows "local action" to occur, which discharges the lead plate.

(4) In the absence of a source of antimony the rate of sulphation, or self-discharge, of the negative plate is negligibly small at all stages of its life.

(5) The bearing of the results obtained on commercial practice and working conditions is discussed.

SPECIAL REFRACTORIES FOR METALLURGICAL RESEARCH.

BY DONALD TURNER, B.Sc. (Tech.).

The properties of refractory materials frequently prove limiting factors in metallurgical research, particularly in investigations conducted at very high temperatures or in which a high standard of purity must be maintained. Difficulties due to refractories have arisen in the course of a number of researches which have been in progress in the Metallurgical Department of the National Physical Laboratory during the past few years.   Materials and apparatus were required possessing, in addition to a high degree of refractoriness, a number of other specific properties relating to strength, porosity, resistance to chemical attack, and thermal endurance.   It became necessary to use special refractory materials, and also to produce articles of special design demanding novel methods of treatment and construction.

The stringent demands made on refractory materials in these researches could not be met by any of the materials available from outside sources. It became necessary, therefore, to devote a considerable amount of study to the properties of various refractory materials, and to carry out investigations relating to their production in the form of suitable apparatus.   Fortunately the Department was in a favourable position to undertake such work.

Investigations had previously been conducted on refractory materials in connection with researches on optical glass,[1] and the experience of high temperature experimental work gained in this way proved valuable in the development of a new technique.   The Department also possessed a considerable amount of equipment which facilitated the progress of the work, especially in its early stages; the high temperature recuperative furnace designed by Rosenhain and Coad-Pryor[2] has been used throughout this work and has proved efficient and satisfactory.

[1] See *J. Soc. Glass Tech.*, **2**, 285, 1918 ; **3**, 93, 1919 ; **4**, 140, 1920.
[2] Rosenhain and Coad-Pryor, *Trans. Cer. Soc.*, **18**, 407, 1918-19.

The present paper describes the materials which have been developed for use in various investigations and the methods of production employed. The work has, in general, been carried out in close collaboration with the workers in the various researches, from whom it has received much help and stimulus, while the successful completion of these researches has been dependent on the development of suitable refractories.

1. The Materials Employed—their Treatment and Preparation.

Aluminous-Clay Mixtures.—For many purposes refractory clays form a suitable material for crucibles and other refractory articles. Their plastic properties when mixed with water enable them to be readily moulded or pressed to any desired shape ; similarly, clay articles may be produced by the well-known method of slip casting. Wherever possible, therefore, in the preparation of refractory articles, it is usual to employ argillaceous materials either as a basis or, in smaller quantities, as a bonding agent for other substances. A highly refractory china clay has been used as the basis of most of the clay refractories used in this work. This material was selected for its purity, high refractoriness, and ease of casting. Considerable experience with this clay had also been gained during research on glass refractories, and crucibles prepared from china clay with suitable "grog" additions had previously been used extensively for temperatures up to about 1500° C.

The use of still higher temperatures for metallurgical research demanded a more refractory material, especially as the limitations in size of the experimental furnaces necessitated the use of thin walled crucibles approximately cylindrical in shape. Two types of melting furnace were available during these researches : the electric graphite ring resistance type, and, in the later stages of the work, the high frequency induction furnace. The use of the former made a cylindrical crucible desirable in order to melt the maximum quantity of material in the relatively narrow furnace space available. With the high frequency furnace a similar shape of crucible has been employed in order to secure the closest possible electro-magnetic coupling between the charge and the furnace coil.

Clay Crucibles for Use at High Temperatures.—Crucibles capable of withstanding a high melting temperature have been prepared from a mixture of 25 per cent. pure alumina and 75 per cent. china clay without grog additions. The usual method of slip casting in coreless plaster of Paris moulds has been employed, small additions of electrolytes (sodium carbonate and sodium silicate) assisting in the deflocculation of the clay slip. The addition of alumina somewhat increases the difficulties of casting, but, by calcining the powder at a high temperature (1550° C.) before admixture with the slip, no cracking or other type of failure takes place during drying or firing. Such crucibles are fired at 1530° C., and may safely be used for temperatures well in excess of 1600° C.[3]

High Temperature Gas-Tight Muffles.—The use of the electric graphite ring resistance furnace makes it necessary to provide an almost gas tight refractory muffle in order to prevent contamination of metal charges by the carbon particles or carbonaceous gases which are evolved from the resistor elements. Muffles, capable of withstanding temperatures of over 1600° C., have been prepared from a mixture of 20 per cent. pure alumina, and 80 per cent. china clay, by the casting method described above. Fired to 1560° C. such muffles give sufficient protection for many purposes :

[3] See also *J. Iron and Steel Inst.*, **121**, 225-304, 1930.

they are probably impervious to minute carbon particles, but where complete protection from carbonaceous gases is necessary a more completely impervious muffle must be employed.

Glaze.—A glaze of the following composition has been evolved to render the muffles, as far as possible, gas-tight.

China clay	40 parts
Quartz	30 „
Felspar	30 „

The materials must be well mixed and fritted at a high temperature (1600° C.) before use. The frit is then crushed to a fine powder, mixed to a slip with 5 per cent. of added china clay, and sprayed on to the muffles, which have previously been fired to 1560° C. The muffles are then again fired at 1610° C. The glaze is very viscous at high temperatures and does not craze. The following tests indicate the efficacy of the glaze on a muffle, 2 inches diameter and 12 inches long.

The muffle at room temperature was connected to a vacuum gauge and exhausted under a powerful pump. The pump was then disconnected, and readings of the gauge were taken at suitable intervals. An increase of pressure corresponding to 1 mm. of mercury was observed after 75 seconds.

Pure iron was then melted in an atmosphere of hydrogen in both types of muffle, a temperature of 1560° C. being maintained for approximately 30 minutes in each case. After the specimens had been cooled and removed from the furnace the carbon content of each sample was determined. The iron melted in the unglazed muffle contained 0·076 per cent. of carbon; that melted in the glazed muffle contained only 0·006 per cent.

Silicon Carbide Clay Mixtures.—Although not suited for contact with molten metals silicon carbide clay mixtures have been used extensively for miscellaneous refractory purposes. It has been found possible to employ the slip casting method using coreless moulds in the preparation of articles from china clay mixtures containing up to 70 per cent. of silicon carbide. The large percentage of silicon carbide which may be added with success in casting of such mixtures is due to the fact of its peculiar formation in flat plates, which considerably assists the stability of the suspension and the strength of the deposit. The grade of silicon carbide usually employed consists of a mixture of particles of all sizes passing a 40 mesh sieve. In certain cases it is necessary to treat the powder magnetically to remove any traces of iron which the material as supplied may contain. A mixture of 60 per cent. silicon carbide, 40 per cent. china clay, fired to 1480° C. has been found suitable for making sleeves, blocks, recuperator tubes, gas burners, etc. This mixture possesses a high mechanical strength, and a good thermal conductivity, and is resistant to severe temperature changes and temperature gradients. Up to the normal firing temperature, the mixture is practically unaffected by an oxidising flame, but, above this temperature, interaction between the clay and silicon carbide appears to produce oxidation of the latter, and the surface slowly deteriorates.

For service at higher temperatures a mixture of 95 per cent. silicon carbide and 5 per cent. china clay has proved satisfactory. This mixture may be moulded without serious difficulty, and the strength of the mixture in the "green" or unfired condition is just sufficient to enable the moulded articles to be transferred to the furnace with reasonable care. An increase in strength in the "green" state may be obtained by the addition of 2 per cent. borax, added in solution; this does not seriously reduce the refractory properties of the material.

Fig. 1.—Small crucible moulds. (1/4 scale.)

Fig. 2.—Large crucible moulds. (1/6 scale.)

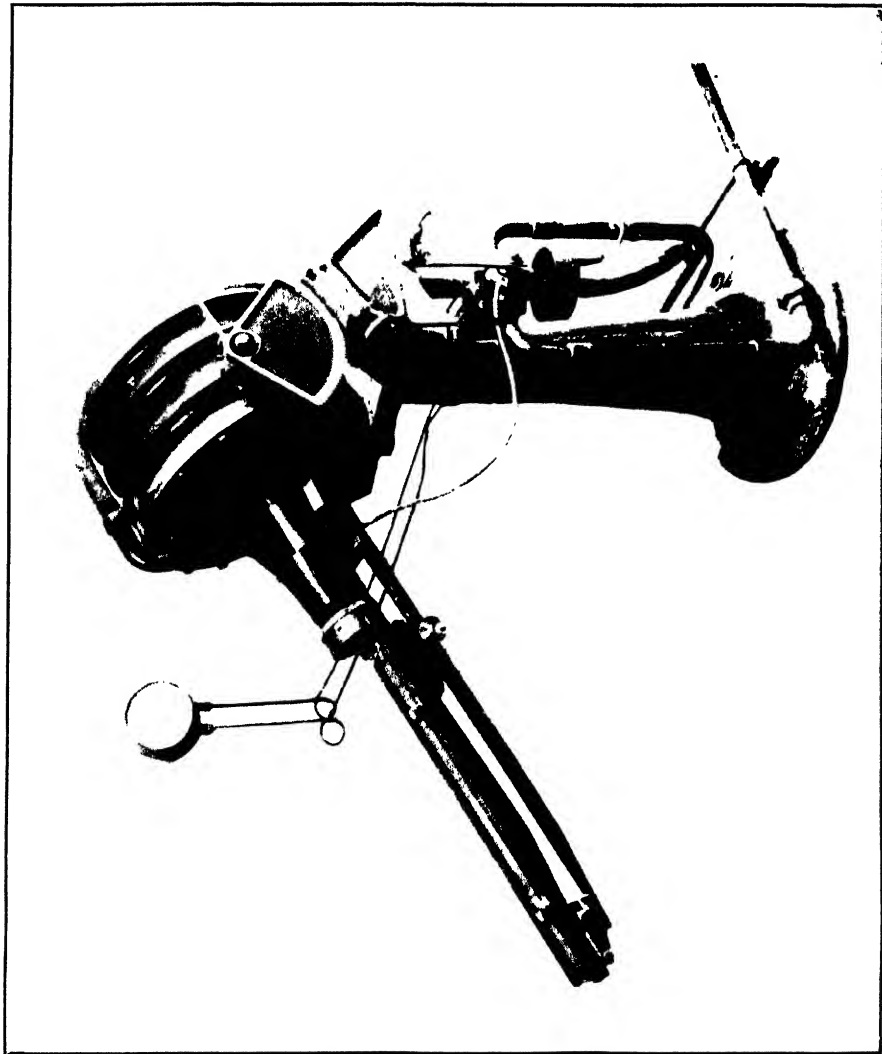FIG. 3.—Extrusion machine.

Non-argillaceous Materials.—Clay mixtures have proved unsuited for crucibles to be used for melting many alloys having a high melting-point, and where alloys of great purity are required. Slight contamination can usually be observed even under normal atmospheric or vacuum melting conditions : a reducing atmosphere of hydrogen is, however, used for the preparation of pure iron alloys, and under these conditions siliceous materials are rapidly reduced. It has been necessary, therefore, to produce crucibles from a variety of materials which possess no plasticity and little bonding power, and a method has been devised whereby it is possible to mould such articles.

Preparation of Crucibles from Non-Plastic Materials.—For the preparation of crucibles from non-plastic materials, a metal mould provided with a removable core is used. Such moulds for small crucibles are shown in Fig. 1. The core, which is slightly tapered, is provided with a flange which fits into a recess at the top of the mould. Filling of the mould is carried out from the bottom.

The refractory material, in powdered form, is mixed with a quantity of water, so as to give it slight cohesion. The quantity required corresponds approximately to the volume of the pores in the material—cracking of the crucible on removal usually indicates an insufficiency of water. This mixture is fed in small quantities into the mould, each filling being tamped down hard by a small wooden rod. This procedure is necessary as the mixture has little or no plasticity : large fillings result in weak places in the crucible from the jamming of the material in consequence of insufficient flow. The usual type of press is useless for this purpose. When the sides and bottom of the crucible are filled, a disc of suitable size is placed over the bottom of the crucible, and the latter, complete with core, is pushed out of the mould. The outside of the crucible is then wrapped with paper, and gently gripped, while the core is removed by a twisting motion.

Crucibles up to 4 inches high and 2 inches diameter are made by this method. Where larger crucibles are required a modified mould is used. This type is shown in Fig. 2. The outer part is in three sections, and a loose brown paper liner is inserted before use. After pressing as before, the crucible is held in position by a flange in the outer section, while the core is unscrewed and withdrawn, the tops of the mould and core being provided with threads for this purpose. The twisting action, combined with a steady pull during withdrawal, leaves a good surface on the interior of the crucible. The outer sections of the mould are then separated and removed, and the paper lining, which prevents any tearing of the crucible during this process is unwrapped. Without this liner the crucible would be split into three parts when the sections of the mould, which make contact over a large area, are pulled away.

The moulds are constructed of aluminium alloy except for the threaded portions of the core, which are of brass, so as to avoid any binding.

Crucibles of Commercial Materials.—Crucibles were first moulded in the above way from a variety of materials, all of commercial quality. In the unfired condition the crucibles are naturally very fragile, but, by careful handling, can be transferred to the furnace and fired. Tap water alone seems to provide sufficient binding power in the " green " condition, but, as a general practice, a little gum tragacanth is added to give additional strength. The crucibles are supported on a loose layer of powdered alumina, sprinkled on a brick, and are fired in a recuperative kiln to approximately 1550° C. The strength of the fired crucibles is good, and few failures have been experienced during the firing period. The

pots are naturally of a somewhat porous nature, but are suitable for all normal melting operations. The following brief details of the fired crucibles may be noted.

Alumina.—This material is supplied in the form of a fine powder. It is a crude material which had been electrically sintered and crushed. The crucibles are hard, fairly fine grained, and yellow-stone in colour.

Magnesia.—Crucibles have been prepared from electrically fused magnesite. The material is obtained in lump form and is crushed in the Laboratory. These crucibles are of a dark brick colour.

Lime.—The manufacture of crucibles from burnt lime necessitated the use of a non-aqueous liquid. The slaked product, may, however, be used.

Chromite.—Crucibles of chromite are strong and fire to a dense black colour. For making the larger sizes of crucible, however, it has been found necessary to fire and crush the material before making it into crucibles as the excessive shrinkage of the raw material otherwise produces cracking.

Crucibles from Pure Oxides.—The crucibles which are described above are made of comparatively crude commercial materials and contain numerous impurities. Such crucibles have been of great service for high temperature melting of metals and alloys where great purity is not required. More difficult conditions, however, have arisen in those researches where even slight contamination of the molten metals had to be avoided especially when melting has had to be conducted in an atmosphere of hydrogen. Under these conditions it has been found that serious amounts of impurities are introduced from crucibles of crude material; for example, the presence of even a small percentage of silica in a crucible may result in the contamination of the melt by silicon. It has been necessary, therefore, to produce crucibles from pure oxides, which are not reduced by hydrogen in contact with metals. Crucibles have been prepared from pure alumina, magnesia and thoria.

Pure Alumina Crucibles.—The pure form of alumina used for these crucibles has been obtained from the British Aluminium Co. in the form of a fine white powder, passing through a 120 mesh sieve. An analysis shows that the only impurity is a trace of iron (less than 0·01 per cent.). The material is made into crucibles in the type of mould described above, but preliminary calcining proved to be unnecessary as very little shrinkage occurred during firing. In the unfired condition the crucibles are very fragile and tend to fall to powder if slightly jarred. They can, however, be safely handled with care. After firing to 1560° C. they are very friable, but hold together reasonably well and are perfectly white in colour.

In spite of their fragile nature these crucibles can safely be used for high temperature melting, if adequately supported in an outer sleeve or jacket. Some trouble was at first experienced in firing the larger sizes of alumina crucible (8 ins. high). It has been found, however, that by subjecting the powder to the action of dilute hydrochloric acid for two or three days,[4] the surfaces of the grains may be modified so as to give sufficient bonding power to prevent the collapse of the crucible during firing.

During firing the crucibles stand on a loose layer of pure alumina. This layer must be of sufficient thickness to permit free movement of the base of the crucible during its firing shrinkage. The crucible must be placed lightly on the loose powder, otherwise this supporting layer tends to adhere both to the crucible and its support, and cracks may be produced. It is also important that the layer should be quite flat; a slight unevenness tends to produce strains in the bottom and cause cracking.

[4] *Z. anorg. Chem.*, **133**, 187, 1924.

Stronger Type of Alumina Crucibles.—While the friable nature of alumina crucibles prepared in this way does not prevent their use for experimental melting, it has been observed that alloys melted in the high frequency induction furnace, frequently contain small particles of alumina. These are presumably mechanically mixed with the charge owing to the friable nature of the crucible, and the violence of the stirring produced by electro-magnetic effects during high frequency melting.

It became desirable, therefore, to produce a crucible of somewhat stronger texture, and it was found that additions of calcium fluoride brought about a marked improvement in this respect. Large additions, however, tended to cause excessive shrinkage and cracking.

Experiments were then conducted to discover the effect of a suitable grading of particles of various sizes. The alumina is received in the form of a powder passing through a 120 mesh sieve, but appears to consist in the main of grains of equal size. By grinding the material in a steel end runner mill for a suitable period, it has been found possible to produce a mixture of grains of various sizes which, when made into crucibles, forms a dense body of considerable strength. Experiments have shown that the period of grinding is not critical, and that no special selection of grain sizes is necessary. The prepared material is considerably finer than would be held by a 200 mesh sieve. Usually a period of three or four hours grinding is sufficient. This is followed by magnetic treatment to remove the iron introduced in grinding. The crucibles are made by moulding as before.

This type of material has also found application in the making of other refractory apparatus. A most useful property from an experimental standpoint is that such apparatus can be drilled or turned in the lathe. Such treatment naturally causes serious wear on the tools employed, but the hardness of the material can be adjusted by suitable regulation of the preliminary grinding process.

Slip Casting of Alumina Crucibles.—The moulding method which has been described does not permit the making of crucibles with a wall thickness less than approximately 1/8 inch. For certain investigations a supply of thin walled alumina crucibles is required. A method for slip casting alumina had been developed for this purpose. The method employed is based on the work of Ruff and his colleagues.[4]

Plasticity is obtained by wet grinding powdered alumina in an end runner mill and subsequently treating the slip, obtained in this way, with hydrochloric or nitric acids at a temperature approaching the boiling-point. The mass then remains in suspension for a considerable period, and can be cast in coreless plaster of Paris moulds. If the slip is prepared with care, the casting will shrink in the mould sufficiently for easy removal and no difficulty is experienced in firing the crucibles.

The main difficulty in this process is that of rigidly maintaining the purity of the alumina. During the grinding process a certain amount of contamination is inevitable. Since, however, siliceous material must be entirely excluded, the usual type of porcelain mill cannot be employed. The use of a steel mill presents advantages ; the iron introduced in this way can be dissolved out during the acid treatment, and subsequently removed. During the acid treatment of the ground material, however, considerable quantities of gas are evolved from the solution of the iron. It is necessary, therefore, to drive off this gas, and remove, as far as possible, the solution containing the iron. Furthermore, the slip must be of suitable acidity before casting.

Preparation of Casting Slip.—The powdered alumina (as received) is

ground in a steel end-runner mill (100 revs./min.) during 4 to 5 hours, each charge consisting of 600 g. alumina and 480 c.c. water. The slip is then treated with excess of hydrochloric acid, and heated to 90° C. until all evolution of gas has ceased. It is not desirable to filter the slip in order to remove the solution containing the iron, but, after allowing it to settle for 12-48 hours, it is possible to pour off most of the supernatant liquid. One or two washings with dilute acid follow, the slip being left to settle and the liquid decanted after each process. The exact amount of acid used and the number of treatments depend on the condition of grinding and the amount of iron present.

Hydrochloric acid and water are then added until a slip of suitable fluidity and approximately of acidity $N/1$ is obtained. This slip can usually be cast without further treatment, but in some cases a second heating to 90° C. for an hour proves advantageous. Rigid conditions of treatment cannot be laid down, and modifications to suit individual cases are required. In particular it has been observed that any cracking of the castings in the plaster mould can usually be cured by increasing the acidity of the slip.

Crucibles prepared in this way and fired to 1560° C. are extremely strong and dense. They have a high pitched "ring" and are comparable in strength with well-fired clay articles. Thin-walled crucibles and other alumina apparatus of more complex shape have been produced by this process, and no difficulty has been experienced in making crucibles up to 14 ins. high and 6 ins. diameter.

Pure Magnesia Crucibles.—Moulded crucibles have also been prepared from pure magnesia. This material is purchased in the form of chemically pure "heavy" magnesium oxide. Two grades of material have been in use, the impurities being as follows:—

	Al_2O_3 and Fe_2O_3.	CaO.	SO_3.
Batch A	0·04 per cent.	0·20 per cent.	1·43 per cent.
Batch B	0·08 ,,	1·46 ,,	0·06 ,,

The latter material was obtained as special "sulphur-free" magnesia, but the use of the former did not prove detrimental to alloys melted in the prepared crucible. The sulphur content of the crucible after firing was 0·005 per cent.

Owing to the excessive shrinkage of magnesia on firing, it has been found essential to heat this material to about 1560° C. before use. The firing is carried out in clay crucibles, painted on the interior surface with one or two coats of aluminium paint. The latter oxidises during the firing operation, interposing a thin protecting layer of alumina between the magnesia and the clay of the container, which would otherwise interact vigorously.

Pure magnesia crucibles are white in colour and are finer in texture and appreciably harder than the original type of pure alumina crucible. As used for experimental work they have proved of sufficient strength, although much more fragile than those prepared from the cruder materials.

Magnesia and alumina crucibles have been developed with the object of producing a container which will prove resistant to the corrosive action of metals at high temperatures, especially under reducing conditions in an atmosphere of hydrogen. In general, it may be said that both these materials proved satisfactory; magnesia is, however, reduced under certain conditions, for example, by molten chromium in an atmosphere of hydrogen and for these alumina proved much more stable. With the

object of producing crucibles of still greater stability, thoria has been used as a refractory.

Thoria Crucibles.—Crucibles have been produced from pure thoria, and have been found to be superior to those of either magnesia or alumina. Metals melted in these crucibles have a cleaner surface, and rarely adhere to the walls. Pure thoria bonds well and gives a dense strong crucible.

Thoria-lined Crucibles.—The high cost of pure thoria renders crucibles of solid thoria very expensive. It has been found possible, however, to coat the interior of the original type of friable pure alumina crucible with a layer of thorium oxide. The thoria is made into a thin paste with a little gum and water and the slip rapidly poured in and out of the fired alumina crucible. One to three coats are given, after which the pots are again fired. A strong inner lining of thoria is produced, which can, if desired, be removed from the outer crucible without damage to the former. Coated crucibles (alumina or magnesia) of this type prove an efficient substitute for the solid thoria crucibles. This method of lining cannot readily be applied to the denser types of crucible owing to the peeling of the coating.

Silica Crucibles.—The preparation of certain iron-silicon alloys required the use of a silica crucible, as it was found that these alloys became contaminated with aluminium when melted in an alumina crucible in hydrogen. Attempts were made to utilise commercial crucibles of fused silica for this purpose, but it was found that these were not sufficiently refractory since the vitreous material shows signs of softening at temperatures below those required. Crucibles suited for this purpose have been prepared from crystalline silica, which, unlike the fused amorphous material, does not soften appreciably until the melting-point is approached. Water ground quartz is first fired to a temperature of about 1550° C. to transform the quartz into its high temperature modifications, as the volume changes associated with these inversions would otherwise be likely to shatter the crucible during firing. After this preliminary treatment the material is crushed, treated magnetically to remove iron, moulded into crucibles and refired.

Other Materials.—The principal materials which have found general application have been dealt with in this section. No mention has been made of zirconia crucibles. Such crucibles have been made and have received consideration, but, in general, it may be remarked that this material is difficult to obtain in a really pure state, and, because of the readiness with which partial reduction of this oxide takes place, it has not been thought suitable for use under the reducing conditions which are usually employed in the preparation of pure metals. Pressed crucibles of pure beryllia, have, however, been prepared by the moulding method by Dr. A. C. Vivian for use in connection with beryllium and its alloys.

2. Adaptations to Special Purposes.

Iron-Oxygen System.—Crucibles made of the oxides, whether pure or crude, as described above, proved incapable of retaining molten oxide of iron. This difficulty was surmounted by F. S. Tritton [5] who devised a method of producing small crucibles of magnesia and zirconia having a vitrified internal surface, using electric arc heating combined with rapid rotation of the material.

[5] *Proc. Roy. Soc.*, **107A**, 287, 1925.

Melting in the High Frequency Induction Furnace.—In the high frequency induction furnace the heat is generated in the metallic charge while the crucible is, as a rule, placed inside a silica tube of comparatively large diameter, which is itself kept cold by the immediate neighbourhood of the water-cooled induction coil.   In these circumstances the crucibles are exposed not only to severe internal heating, often very rapidly applied, but also to a very steep temperature gradient.   While crucibles of some of the materials employed, owing perhaps to their low thermal expansion and open, porous, texture are capable of withstanding these severe conditions, in other cases difficulties from cracking have been serious.   This applies particularly to the thin walled crucibles of relatively large size made of aluminous china clay such as have been used in connection with the researches on the alloys of nickel and chromium and for certain steel melting experiments.   A method of supporting these crucibles in such a manner as to prevent the outflow of molten metal even if the crucible itself becomes cracked, has, therefore, been developed, and this has also proved useful in furnishing a means of mechanically supporting the comparatively weak crucibles made of some of the pure oxides.

The method adopted has consisted in placing the crucible proper inside an outer crucible or sleeve made of a very strong refractory material. For this purpose a mixture of silicon carbide with 40 per cent. of china clay has been employed.   These sleeves have been produced by slip casting and have been prepared of satisfactory shape for utilising as fully as possible the available space within the silica tube container.   The crucible proper fits very loosely within these sleeves, leaving room for a packing of loose alumina powder.   It is necessary to give this alumina powder a preliminary calcining treatment at a temperature of about 1550° C. since otherwise it is found that, when the crucibles are heated there is a tendency for the alumina powder to be ejected.   As a rule, the powder is merely consolidated by lightly tapping the sleeves during the packing process. In certain special cases, however, the powder is tamped more firmly into position and the sleeve with its crucible and powder packing is then again fired to a temperature of 1550° C.   In these circumstances, the sleeves which have previously been fired only to 1480° C., undergo a slight contraction which consolidates the powdered alumina between it and the crucible.   The slight state of internal pressure resulting from these actions tends to prevent the opening of any cracks which may subsequently be formed in the crucible proper.

This arrangement of crucible, packing and sleeve, has proved highly successful, since it has, in almost every instance, prevented the escape of metal from the crucible.   It must be remembered that in this outer packing there is a fairly steep temperature gradient, and that consequently any small quantity of metal which passes through a crack in the crucible is rapidly chilled and further efflux is prevented.   At the same time, the comparatively loose packing of alumina serves to give a certain measure of heat insulation to the crucible and its contents which improves the efficiency of working of the furnace.

Crucibles for Research on Alloys of Iron and Manganese.—The pure manganese used in the research on these alloys is prepared by distillation in vacuo.   Crucibles of pure magnesia, alumina, or thoria are sufficiently resistant for use in this process, and have also been employed for the melting of iron-manganese alloys.   Under vacuum conditions, however, even crucibles of relatively crude magnesia or alumina are only slightly attacked by either iron or manganese alone, but when alloys of the two metals are

melted large quantities of silicon are taken up. The following figures are typical :—

Magnesite Crucible used for melting
    pure iron

                Silicon content of iron
                    after melting   .   .   0·004 per cent.

Magnesite Crucible used for melting
    alloys of iron and manganese

                Silicon content of alloy
                    after melting   .   .   0·69 per cent.

The difficulties connected with the research on the alloys of iron and manganese are increased by the volatility of manganese, and special problems have arisen in regard to the protection of thermo-couples used for temperature measurements in this work. The production of impervious tubes for this purpose is referred to later.

3. Special Processes.

Tubes for the Protection of Thermo-couples.—The protection of thermo-couples used for high temperature measurements from contamination by metals, metallic vapours, etc., is very important. Tubes to serve as protecting sheaths have been made from a variety of materials and by the following methods.

Extrusion Machine.—Small tubing is usually produced by extrusion through suitable dies, and a special extrusion machine, designed by Mr. H. P. Bloxam, has been made in the Metrology Department of the Laboratory for this purpose. This machine, which is illustrated in Fig. 3, is actuated by a hydraulic ram, and has been designed to have the maximum flexibility of operation in order to meet the varied requirements of experimental work. It can be adjusted to operate at any desired angle from the vertical, so that the extruded product may, if necessary, be supported by an inclined plate-glass receiving plate, so adjusted to suit the coefficient of friction of the tube or rod against the glass, that the latter will slide down the plate without exerting any pulling or pushing action on the material emerging from the die. This method has proved successful. The machine will operate in a horizontal or vertical position and can also be readily used as a press. The plunger, which is made of stainless steel to resist corrosive action, slides in an outer cylinder, which is provided with an interchangeable lining of softer material. In this way wear is mainly confined to the outer sleeve, which may readily be replaced. Wear has been reduced to a minimum, however, by the use of a very small clearance between the plunger and sleeve so that the machine is to a large extent " self-cleaning."

Extrusion of Non-plastic Materials.—The success of the extrusion process depends on the plasticity of the material, and has, therefore, usually been confined to the production of tubes from clay mixtures. In this work it has been necessary to apply this method to non-plastic materials. Additions of gum to such substances, so as to produce the necessary plasticity are not satisfactory ; either the tube produced is too soft to retain its shape, or the liquid is squeezed out first, and the refractory is left in the chamber as a hard mass.

Success has been attained by the use of a quick drying cellulose acetate solution. This is mixed with the powdered material to obtain plasticity, and a stream of air is directed on to the tubing as it leaves the extrusion

press.   The volatile constituents of the solution evaporate rapidly and the tubing hardens almost immediately.   A cellulose acetate solution of suitable properties which has been obtained commercially has the following composition :—

> 100 g. Cellulose Acetate (Medium viscosity).
> 200 „ Industrial Spirit.
> 200 „ Benzol.
> 700 „ Acetone.

This solution is rather weak, but proves satisfactory.   It is advisable, however, to mix the solution with the refractory material and allow it to harden, finally mixing with a further quantity of acetate before extrusion An excess of solution is used, and the mass kneaded by hand until enough evaporation has taken place to yield a body of suitable plasticity.

Tubing made by this method can be fired within an hour or so of manufacture, and is remarkably strong and even flexible in the unfired state.   The method can be applied to the production of tubing from any material.   Closed-end tubes may be made by pressing a mixture of the tube material and acetate solution into the end of a tube which has been moistened with acetone.   Slight pressure and trimming by means of a knife produces an end which forms a sound integral part of the tube.

Tubes and rods have been produced in this way from a great variety of materials, and ranging in size from small clay insulating tubes of 1/20 in. bore to pure alumina tubes of about 1 inch diameter for use in the production of single crystals of pure metals.

High-Temperature Thermo-couple Protecting Sheathings.—The selection of a material for use in the form of a protecting sheath for thermo-couples at high temperatures depends essentially on the conditions under which it is to be used.   Under oxidising conditions, where the only source of contamination is the molten metal in which the thermo-couple is immersed, a fairly porous clay tube is usually sufficient to prevent penetration by the metal.   Frequently, however, a sheath of an impervious nature is desired.   Fused silica may be employed for short periods at temperatures in the region of 1300° C.-1500° C. but is insufficiently refractory for prolonged use at high temperatures.

Ball Clay Alumina Tubing.—Tubing extruded from a ball clay mixture containing 10 per cent. of added alumina was used extensively for the earlier work on iron alloys, when the melting operation was carried out in air or in an atmosphere of nitrogen.   When fired at 1560° C. these tubes vitrify and are moderately gas tight.   It is curious that sudden or very slow immersion in a hot furnace does not crack this tubing, although an intermediate rate of heating is liable to do so.   Lengths of this tubing can be joined, or the ends sealed, in an oxy-coal gas flame.   Such tubes cannot, however, be used in molten iron-manganese alloys in an atmosphere of nitrogen.   Serious corrosion takes place, increasing as the percentage of manganese in the alloy is raised.

The making of these tubes has been discontinued.   Satisfactory tubes of this type of an impervious nature but subject to the same limitations can now be obtained commercially.

Protective Sheathings for use in Reducing Atmospheres.—It has previously been explained that the use of siliceous materials in contact with metals in hydrogen at high temperatures results in contamination of the metal by silicon.   Thermo-couple tubes of the types described above are, therefore, useless under these conditions.   Sheaths of pure alumina, magnesia, or thoria have, however, proved successful.

Non-porous Sheaths suitable for use in the Investigation of Manganese Alloys.—The volatility of manganese at high temperatures necessitates the use of a substantially non-porous thermo-couple sheath. Furthermore, the use of an atmosphere of hydrogen precludes the use of materials of a siliceous nature.

Lime Alumina Tubing.—Experiments have been carried out on a series of fluorspar-alumina mixtures which can be vitrified at a temperature, which, while above those required for experimental work, can be readily attained in the Laboratory. Mixtures varying about a ratio of 60 parts calcium fluoride to 100 parts of alumina have been found to vitrify and soften at about 1690° C. The vitrified material is crushed, made into tubes, and again fired. Tubes thus produced can be used up to 1600° C. Preliminary experiments were made, using natural fluorspar, and tubes produced from this mixture were almost gas-tight. A tube 15 ins. long and 3/16 in. in bore, immersed in a furnace at 1560° C. surrounded by an atmosphere of hydrogen, showed, on evacuation, a leak producing a rise of pressure of only 1 mm. of mercury in half a minute. Such tubes also showed practically no sign of corrosion when immersed in molten iron or manganese, but, unfortunately, the silica present in the commercial fluorspar resulted in corrosion in contact with alloys of these metals. By the use of pure calcium fluoride it is possible to produce gas tight tubes which will resist corrosion in these circumstances; the firing temperature of the silica-free mixture proved so critical, however, that difficulty has been experienced in producing a sufficient supply of these tubes.

It is possible to make use of the non-porous " Pythagorus " (siliceous material) tubing fitted with a tip of pure alumina for the protection of thermo-couples under such conditions. Pythagorus tubing is, however, fairly rapidly corroded by manganese vapour, and the thermal lag due to the extra thickness of refractory wall tends to produce serious temperature errors.

Glazed Alumina Tubing.—A non-porous tube of pure alumina would form an ideal thermo-couple protecting sheath for use under the stringent conditions imposed by the melting of iron-manganese and other alloys in hydrogen, and attempts have been made to glaze, by direct fusion, the hard alumina body which has been described above. It has been found possible to glaze in this way the surface of small alumina tubes in the oxy-hydrogen flame. This method has been developed in collaboration with Mr. F. Adcock.[6]

The tubes are first fired to approximately 1800° C.-1900° C., straightness of the tubes being maintained by careful packing in powdered alumina. They can then be glazed by careful heating in the oxy-hydrogen flame. The preliminary firing proves necessary because it causes the material to shrink so far that the strains set up in fusion by local shrinkage are very much reduced. When glazed, these tubes are not unduly sensitive to rapid temperature changes and are almost impervious. Tubes about 1/10 in. diameter, 1/20 in. bore, and several inches in length have been successfully produced, and the method is now being extended to the production of tubes 3/16 in. diameter and 18 ins. long. The tubes so far prepared in this large size show a slight leak under a vacuum, but it is expected that a further improvement of the fusion methods will overcome this defect.

Production of Moulded Articles of Complex Design.—Some of the crucibles used in the determination of the melting-point of pure iron by

optical methods, by Jenkins and Gayler [7] are of complex design, and a brief description of the technique of their production is given below.

Moulded bodies of non-plastic materials possess little strength in the unfired state.   The design of the moulds used, and the methods adopted for the removal of the crucibles, etc., in such cases require careful consideration.   The general principle to be observed is that no part of the article should at any time be submitted to a tensile stress.   A typical example of these crucibles is shown in section in Fig. 4, and the mould employed for the production of this crucible is shown in Fig. 5.   The pots are made by ramming the moist powder in the usual way, but the chief difficulty lies in the successful extraction of the crucible from the mould.   The crucible is removed as follows :—The mould is held in a screw press which exerts a downward push on the top of the central tube by means of the rod 1.   The annular core can then be pulled out by means of lifting screws without strain on the central tube.   At this stage the rod 1 can be removed and the centre pin 3 withdrawn from below.   The crucible is then pushed out of the mould by means of the bottom plate 4, the latter being then removed. In this way all portions of the refractory article are sustained in slight compression during the removal process, and the risk of fracture is reduced to a minimum.   This general principle is adopted in the production of all moulded articles.

Reference has been made above to the recuperative furnaces which have been used for the firing of refractory articles.   The recuperator tubes for these furnaces are slip cast from a mixture of 60 per cent. silicon carbide, 40 per cent. china clay.   This composition has proved highly efficient for the purpose because of its strength and good thermal conductivity.   The earlier types of cast iron gas burners have also been replaced by burners which are slip cast from a similar silicon carbide-china clay mixture.   A description of this furnace has been given elsewhere.[2]

Photographs of a number of refractory articles prepared in the Laboratory are included in Figs. 6-8.

The author wishes to acknowledge the help and encouragement given by Dr. W. Rosenhain, F.R.S., under whose general supervision the work has been carried out.

[7] *Proc. Roy. Soc.*, **129A**, 91, 1930.

VAPOUR PRESSURE AND HEAT OF DILUTION.— PART VIII. HEAT OF DILUTION OF CANE SUGAR IN AQUEOUS SOLUTION AND OF UREA AND CALCIUM CHLORIDE IN ALCOHOLIC SOLUTION.

By R. B. Vallender and E. P. Perman.

The method used in the present work was, in essentials, that designed by Harrison and Perman,[1] and improved upon in minor details by subsequent workers.

Difficulty has been encountered by previous workers, and also in the

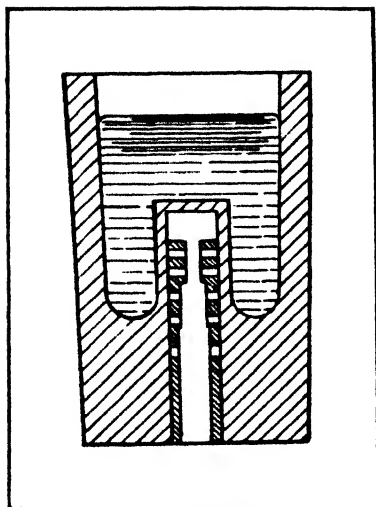[1] *Trans. Far. Soc.*, **23**, 7, 1927.

FIG. 4. Section of crucible for optical determinations of temperatures with baffle pieces in position.
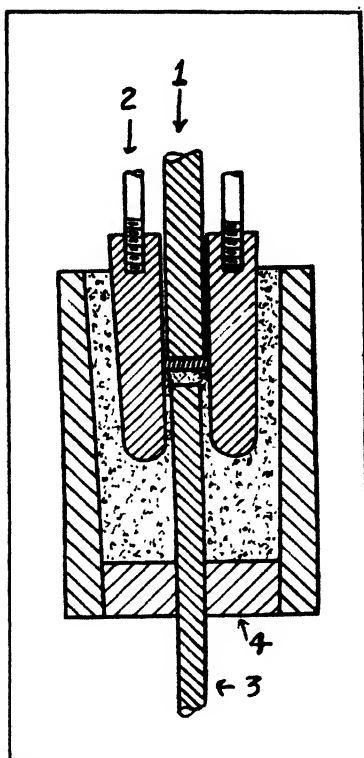

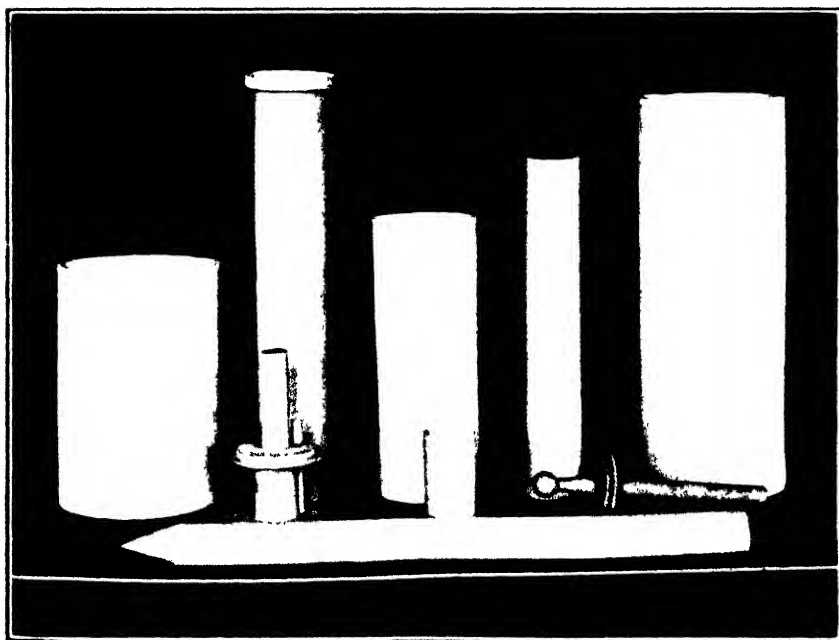FIG. 5. Mould for making crucible shown in Fig. 4.

FIG. 6.—China clay-alumina refractories, muffles, crucibles, etc. (1/6 scale.)
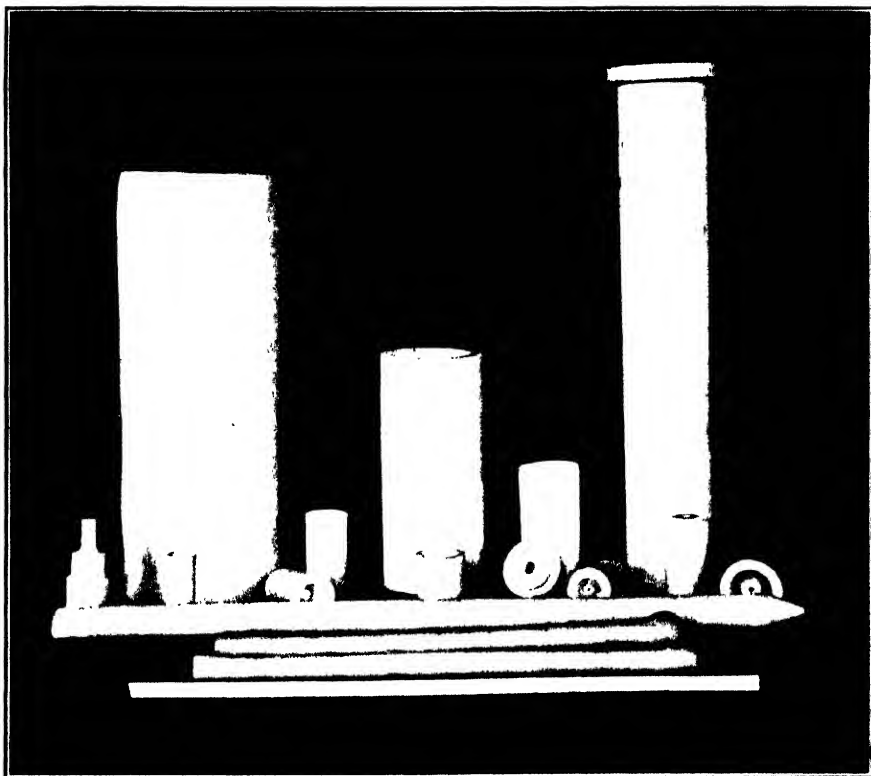
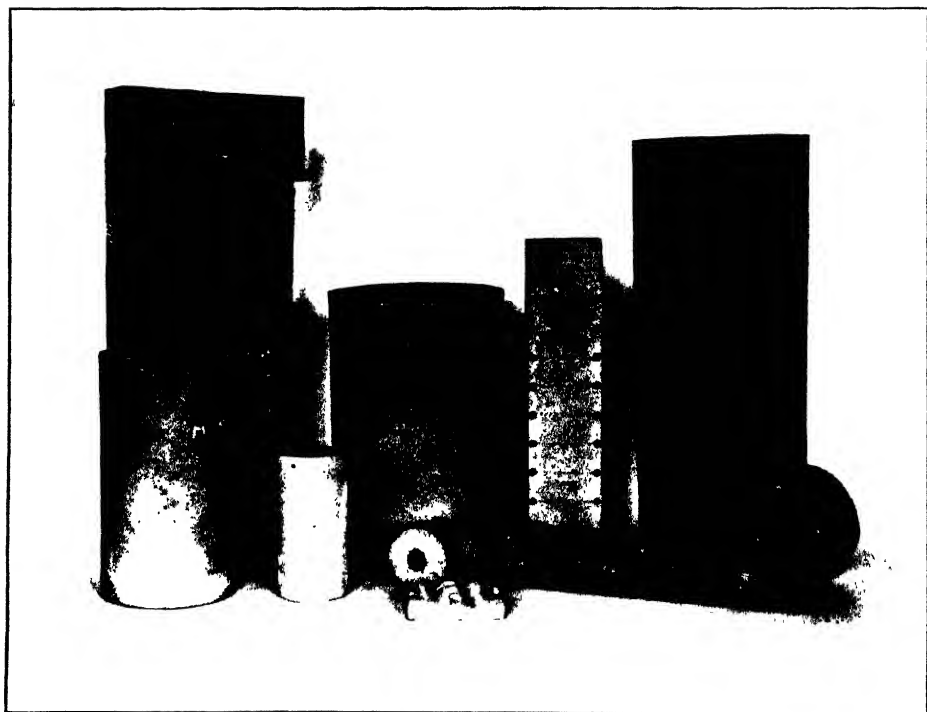FIG. 7.—Pure alumina refractories. (1 5 scale.)

FIG. 8.—Silicon carbide-china clay sleeves, furnace parts, etc. (1/6 scale.) (See page 124.)

present work, when using very concentrated solutions, many of which are very viscous, especially at the lower temperatures, so that a large quantity of heat is generated by the stirring. Now if this heat is to be only just sufficient to balance that lost by conduction etc., the stirrer can only be rotated slowly, and thorough and rapid mixing are then impossible, the solution taking 30 minutes or more to come to equilibrium. More rapid stirring can only be made possible then by increasing the heat losses. A piece of thick copper wire introduced into the air space above the solution through the stopper of the inlet tube of the Dewar flask was found to be fairly effective for temperatures of 40° or 50° C., but for lower temperatures the method of experiment had sometimes to be modified, as will be described later in connection with cane sugar.

Another difficulty previously encountered has been that very concentrated solutions tended, when stirred, merely to rotate as a whole, while the added solvent rose to the surface and did not mix for some time. The stirrer used in the present work proved more efficient in this respect, but in order to increase the efficiency a long glass rod was immersed vertically in the solution through the inlet tube; this served to break up the mass of liquid, and to secure more rapid mixing, though at the same time it increased the amount of frictional heat generated.

A. Cane Sugar in Aqueous Solution.

The cane sugar used was the purest obtainable. It was first thoroughly dried by heating for several hours in an oven. Solutions were made up by weighing out accurately the requisite quantities of sugar and pure distilled water, and a check was kept on the concentration during a series of experiments by means of the density, accurate values of which have been determined over large ranges of temperature and concentration by various workers.

At the higher temperatures the usual method was used; at the lower temperatures, however, owing to the difficulty found in balancing the frictional heat, it was decided not to attempt this, but to secure thorough and rapid mixing, and consequently shorter experiments, by means of rapid stirring, and to estimate previously the extra heat generated which was not balanced by the radiation and conduction losses. Preliminary experiments showed that the rise of temperature produced by the stirring was very regular, and sensitive to small changes in the speed of the stirrer.

To carry out an experiment, therefore, the temperature of the solution was brought below that of the thermostat, and the stirrer set at a rapid speed; the temperature was then noted at intervals of a minute, and the steady rise due to the stirring thus obtained. When the temperature reached that of the thermostat, the dilution was carried out and the temperature readings continued every minute until the rise again became uniform. The mixing was now complete, and the actual rise of temperature due to the dilution could be obtained with accuracy. The time taken for complete mixing was never more than ten minutes by this method, and, except for the most concentrated solutions, rarely more than two or three minutes.

For the electrical reproduction of the heat in the above method a rise of temperature of rather more than that due to the dilution was timed in the usual way, and the rise then corrected for stirring. By proportion the time required for the actual rise was then calculated. The measured rise was arranged so that, after correction, it was as near the actual rise as possible. The rate of stirring was carefully checked two or three times during an

experiment; any variation was thus immediately detected, and, if necessary, the experiment repeated.

The results obtained by this modified method are in good agreement with those of Orson Wood[2] and of Miss Hunter.[3]

An attempt was made to obtain the heat of dilution of cane sugar at 0° C. For this purpose the heater, regulator, and stirrers were removed from the thermostat, and the latter packed with small pieces of ice until the apparatus was completely covered. A thick layer of felt was then placed on top, with holes for the various tubes leading into the Dewar flask. Owing to the packing round the sides of the thermostat, it was found necessary to renew the ice only every two days, and the solution could be kept nearly at zero as long as required. A small rise took place overnight owing to conduction along the tubes entering the flask.

In this series of experiments the general method was impossible, as the solution gained heat both by conduction and by stirring; the above method was therefore used. The water used for the dilutions was first cooled down several degrees below zero by immersion in a freezing mixture; just before it was required, the pipette was filled and weighed as rapidly as possible, and the dilution then carried out. The pipette was encased in a thick layer of cotton-wool to lessen the rise of temperature by external heat As long as the water was run in below 4° C.—the temperature of maximum density of water—a smaller weight of water than that run in was at first forced over from the dilution vessel into the flask; then, on cooling to 0°, a further small quantity was forced over, until finally an equal weight had been added. If the water run into the dilution vessel was above 4°, a slight contraction would occur on cooling, which would cause errors. Usually, however, if the process of filling and weighing the pipette and carrying out the dilution was rapid, the temperature of the water remaining in the pipette afterwards was found to be little more than 0°. A few small pieces of pure ice added to the water in the pipette before weighing assisted in keeping the temperature low.

At 0° C. the range of concentration in which the heats could be measured was considerably smaller than at the other temperatures. This was owing to the lower solubility, and to the fact that the heats obtained were considerably lower for a given concentration than at the higher temperatures, so that they became too small for accurate measurement at a fairly high concentration.

In all, the heats of dilution of cane sugar were measured at five temperatures—0°, 20°, 40°, 60° and 80° C.—and over a range of concentration extending from near saturation down to about 20 to 25 per cent. (except at 0°). At 80° C. solutions within about 8 per cent. of saturation were so viscous that it was found impossible to obtain any consistent results with them.

The results are shown in Table I. Concentrations are expressed as "grams per 100 grams of solution" and as the ratio of the number of molecules of solute (n) to the number of molecules of solvent (N).

Discussion of Results —Heats of dilution of cane sugar have been previously measured by several workers. Stackelberg[4] and Ewan[5] obtained a few values at room temperature, both by making very large dilutions. Porter[6] gives a series obtained at 20° C. by Orson Wood. Miss Hunter[3] measured the heats at several concentrations and for temperatures between

[2] *Trans. Far. Soc.*, **13**, 123, 1917.   [3] *Ibid.*, **22**, 194, 1926.
[4] *Z. physik. Chem.*, **26**, 533, 1898.   [5] *Ibid.*, **14**, 409, 1894.
[6] *Trans. Far. Soc.*, **13**, 123, 1917.

TABLE I.—CANE SUGAR.

Temp. °C.	Concentration—Grms per 100 gms. of Solution.	n/N.	Heat of Dilution per Gram of Water Added (Cal.)	Temp. °C.	Concentration—Grams per 100 gms. of Solution.	n/N.	Heat of Dilution per Gram of Water Added. (Cal.)
0	58·94	0·07554	− 0·53	40	31·66	·02436	·26
	56·98	·06969	·43		28·66	·02114	·23
	55·03	·06440	·38		23·86	·01649	·17
	51·27	·05538	·28		18·93	·01228	·12
	49·40	·05137	·25				
	47·39	·04741	·18	60	67·97	0·11170	− 2·16
	45·31	·04360	·15		66·23	·10320	2·00
					64·59	·09601	1·82
20	63·39	0·09111	− 1·68		63·23	·09048	1·75
	61·82	·08521	1·52		63·07	·09015	1·73
	60·32	·07998	1·39		61·77	·08504	1·63
	56·51	·06837	1·19		59·78	·07823	1·53
	55·05	·06446	1·06		58·90	·07543	1·43
	53·62	·06085	0·92		56·67	·06882	1·26
	52·20	·05748	·86		53·83	·06135	1·17
	47·79	·04816	·65		52·50	·05817	1·10
	46·49	·04571	·57		51·24	·05531	1·03
	41·20	·03687	·40		49·99	·05260	0·96
	40·07	·03520	·37		47·14	·04693	·81
	34·84	·02814	·26		44·60	·04236	·73
	30·18	·02275	·21		41·95	·03803	·59
	25·88	·01838	·13		39·38	·03419	·54
	22·39	·01518	·083		36·91	·03079	·48
	18·99	·01234	·068		33·24	·02620	·36
					28·72	·02119	·28
40	66·75	0·10560	− 2·48				
	63·99	·09340	1·94	80	68·79	0·11600	− 2·02
	62·43	·08746	1·67		66·35	·10380	1·87
	60·81	·08166	1·48		63·94	·09335	1·75
	59·26	·07654	1·39		61·59	·08439	1·64
	57·75	·07194	1·33		59·33	·07678	1·48
	56·26	·06769	1·17		50·67	·05406	1·14
	54·80	·06381	1·12		46·82	·05020	0·98
	47·03	·04672	0·70		43·83	·04107	·79
	45·78	·04445	·64		42·23	·03847	·73
	38·24	·03249	·45		36·10	·02973	·54
	37·02	·03092	·40		29·91	·02246	·37
	34·48	·02770	·34		23·52	·01618	·19

12° and 30° C., while Downes and Perman, in some preliminary work, obtained a series of results for temperatures from 40° to 80° C. These, however, have not been published. There is some discrepancy between the results of the various workers.

The main features of the above results are the small values obtained for all the heats, which were never greater than 3 calories per gram of water, the very low values obtained at 0° C. and the crossing of the heat-concentration curves at high concentrations. The curves for 20°, 40°, 60° and 80° all intersect at very nearly the same point, at which the concentration is 62 to 63 per cent. and the heat about 1·7 calories. The effect of temperature upon the heat of dilution, at all times small in the case of sugar, thus disappears entirely here. Payn and Perman [7] found a similar crossing for hydrochloric acid solutions at 60° and 70° C.

[7] *Trans. Far. Soc.*, **25**, 599, 1929.

The heat of dilution-temperature graph shows at low concentrations a curvature between 0° and 20° C., and then a very gradual linear rise to 80°. As the concentration increases, the curve between 0° and 20° becomes steeper, while the linear portion between 20° and 80° at first become steeper, and then approaches a horizontal straight line. At 62½ per cent. a minimum appears, and above this concentration the curvature increases rapidly. The values obtained at 0° are to some extent borne out on this graph by the results of Miss Hunter; [3] these are in fair agreement with our curves, and show a tendency at each concentration up to 50 per cent. to curve down to low values at 0°. At the highest concentrations, however, where the heat-temperature graph shows the greatest curvature between 0° and 20°, no values at the intermediate temperatures were available, except by rather uncertain extrapolation.

Some idea of the general agreement between the results of different workers is given by the Table II. for 20°; it is seen that the results obtainedf by us for 20° are in good agreement with those of Wood [2] at 20' and o Miss Hunter [3] at 18° and 22°.

TABLE II.—CANE SUGAR — 20 C

Concentration gms./100 gms.	Vallender and Perman.	Wood.	Stackelberg.	Miss Hunter. 18°.	22'
66·1	2·00 *	—	2·00	–	
57·8	1·22	1·12	-	1·13	1·22 *
50·0	·73	-	---	·70	·79
40·6	·39	·42	—	·36	·43
33·9	·245	·245	·	·24	·26
25·5	·13	·11	·	·11	·12
23·5	·11	·09	· ·	·09	·105
21·5	·09	·07	·	·08	·09

B. Urea in Alcoholic Solution.

In previous determinations of heats of dilution, aqueous solutions have been invariably dealt with. MacInnes and Braham [8] and Pratt [9] measured a few heats of dilution of alcohol in water, but no alcoholic solutions appear to have been investigated. Vapour pressures of some alcoholic solutions have, however, been measured by various workers, including Price,[10] who investigated urea solutions; it was with the object of comparing with the results of the latter that the present series was carried out.

The urea used was Messrs. Hopkin and Williams' purest. This was dried in a vacuum desiccator over phosphorus pentoxide for several days, and the purity then tested by a number of accurate melting-point determinations, a cooling curve being constructed for each sample. The melting-point in each case was 132·0° C.

Ordinary laboratory alcohol was used for the series ; this was dried by the use of lime in the manner described by Miss Hayward and Perman,[11] and a product of mean density 0·78509 obtained.

Solutions were made up accurately at the concentration required. A rough check on the concentration during a series could be kept by means

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* Extrapolated values.
[8] J. Amer. Chem. Soc., 39, 2110, 1917.
[10] J.C.S.(T.), 188, 1915.
[9] J. Franklin Inst., 185, 663, 1918.
[11] Trans. Far. Soc., 27, 59, 1931.

of the density, a few values of which were determined by Price.[10] Owing to the low specific heat of alcoholic solutions, the heat generated by the stirrer was at all temperatures much greater than with aqueous solutions, and the general method of balancing the heat losses was therefore impossible. The modified method described for sugar at low temperatures was again made use of.

The heats of dilution were measured at 30°, 40° and 50° C. Owing to the slight solubility of urea in alcohol, the series were short, especially at 30°, but sufficient results were obtained to compare with the vapour pressure measurements of Price.

All the values obtained were thermodynamically positive, i.e., the solution cooled on dilution, as was found by Perman and Lovett[12] for aqueous urea solutions. The heat in every case was extremely small, the value never exceeding 0·45 calorie per gram of alcohol. While, therefore, the accuracy obtained was not quite as great as in the case of cane sugar, the results are more accurate than would be expected from the magnitude of the heats. This was due to the small specific heat of the solutions causing a considerably greater change of temperature on dilution for a given weight of added solvent than for the sugar solutions. Further, owing to the urea solutions being very much less viscous than the latter, the solvent and solution were thoroughly mixed immediately, and the change of temperature was sharp and generally complete in the first minute after dilution. It could, therefore, be estimated with great accuracy.

The results are shown in Table III. ; the curves obtained from them are similar to those for several aqueous solutions, and present no unusual features.

TABLE III.—UREA IN ALCOHOL.

Temp °C	Concentration Grams per 100 gms of Solution.	n N	Heat of Dilution per Gram of Alcohol Added (Cal.)	Temp °C	Concentration—Grams per 100 gms of Solution.	n N	Heat of Dilution per Gram of Alcohol Added (Cal.)
30	5·558	0·04511	+0·095	50	8·887	0·07482	+0·441
	5·361	·04343	·090		8·594	·07200	·426
	5·183	·04191	·082		8·288	·06928	·385
	4·784	·03852	·050		7·981	·06649	·369
	4·593	·03694	·059		7·699	·06395	·331
	4·434	·03558	·048		7·435	·06159	·292
	4·207	·03418	·044		7·178	·05924	·279
					6·912	·05693	·255
40	7·679	0·06377	+0·286		6·667	·05478	·231
	7·483	·06201	·266		6·314	·05166	·201
	7·250	·05992	·246		5·547	·04502	·140
	6·999	·05771	·221		5·210	·04214	·134
	6·247	·05110	·162		5·006	·04040	·121
	6·021	·04911	·146		4·691	·03782	·099
	5·609	·04565	·128		4·512	·03623	·091
	5·411	·04386	·114		4·249	·03402	·084
	5·035	·04064	·095		4·091	·03271	·071
	4·506	·03618	·078		3·688	·02936	·065
	4·049	·03236	·059				

[12] Trans. Far. Soc., **22**, 1, 1926.

C. Calcium Chloride in Alcoholic Solution.

For this series Kahlbaum's "medium granular" calcium chloride was used. Solutions were made up roughly at the required strength, and an accurate volumetric chloride estimation carried out on a sample. At 50° and 60° frequent estimations were made during the series of the concentration of the solution, in order to detect any changes due to evaporation of alcohol; these were, however, found to be negligible.

At every temperature it was again found impossible to use the general method of experiment; even at 60° a moderate rate of stirring produced a considerable rise of temperature.

Measurements were carried out at 20', 30', 40', 50' and 60° C.; the heats were all thermodynamically negative, as for aqueous calcium chloride solutions. They were considerably higher than those for cane sugar or urea, and could therefore be estimated with greater accuracy. The curves obtained are very similar to those for the corresponding aqueous solutions; at all five temperatures they lie very close together, and it was found impossible to plot them on the same graph. The full results are given in table IV.

General Accuracy of the Method.

The accuracy of the apparatus has been previously estimated at about 1 per cent., but up to the present nearly all the substances investigated have had large heats of dilution. The majority of the heats measured in the present work were, however, very small, and consequently the possibility of error in their measurement was somewhat increased.

The chief source of error lay in the reading of the temperature change on the Beckmann thermometer. This could be determined by means of a lens accurately to 0·001°; the changes, however, were generally less than 0·1°, so that the possible error was at least 1 per cent. The temperature changes could be made greater only by increasing the weight of solvent added for a dilution. This would involve larger concentration changes during an experiment, and there would then be an error in determining the exact concentration at which the heat was produced. It was considered advisable, therefore, never to add more than about 30 grams of solvent for a dilution.

Of the other data required for measuring the heats, the weight of solvent added was correct to at least 1 in 1000, the current and potential difference to 0·0001 unit, and the time of heating to at least 1 in 200, so that the errors in these are negligible.

The extreme viscosity of the more concentrated cane sugar solutions increased the time taken for the solution and solvent to mix, and any small errors made in balancing the heat losses therefore became important. This retardation of the experiment was, however, never serious, except for the very concentrated solutions at first used at 80°. For these, as mentioned previously, no consistent results were obtained owing to the excessive time taken for mixing. Otherwise the error from this source was very slight.

Another possible cause of error at first was to run the solvent into the dilution vessel at too high a temperature; this was obviated by a modified form of pipette, which allowed of the introduction of a thermometer. Nevertheless, a test was made by filling the Dewar flask with water at the temperature of the thermostat, and then running in quantities of water from the pipette at temperatures several degrees above and below the

TABLE IV.—CALCIUM CHLORIDE IN ALCOHOL.

Temp. ° C.	Concentra- tion –Grams per 100 gms. of Solution.	n/N.	Heat of Dilution per Gram of Alcohol Added. (Cals.)	Temp. ° C.	Concentra- tion –Grams per 100 gms. of Solution.	n/N.	Heat of Dilution per Gram of Alcohol Added. (Cals.)
20	17·76	0·0895	− 3·98	40	11·96	0·0563	1·87
	16·62	·0826	3·51		11·44	·0536	1·70
	15·82	·0779	3·18		10·52	·0487	1·47
	15·69	·0771	3·02		10·40	·0481	1·34
	14·89	·0725	2·85		9·17	·0419	1·11
	14·73	·0716	2·71		8·45	·0383	0·88
	13·96	·0673	2·30		7·23	·0323	·69
	13·12	·0626	2·09		6·60	·0293	·56
	12·32	·0582	1·78		5·79	·0255	·47
	11·56	·0542	1·51				
	10·81	·0502	1·43	50	25·18	0·1395	− 9·88
	10·07	·0464	1·18		24·30	·1330	9·23
	9·35	·0428	1·04		23·37	·1265	8·64
	8·65	·0392	·80		22·11	·1177	7·70
	8·00	·0360	·77		21·13	·1110	7·18
	7·14	·0319	·61		20·86	·1092	6·86
	6·33	·0280	·51		19·82	·1024	6·20
	5·64	·0248	·43		18·84	·0962	5·64
	4·78	·0208	·28		17·95	·0907	4·77
	4·15	·0180	·24		17·10	·0855	4·27
					16·26	·0805	3·77
30	20·27	0·1054	− 5·46		15·42	·0756	3·43
	19·52	·1005	5·11		14·65	·0712	3·02
	18·70	·0952	4·84		13·89	·0669	2·62
	17·86	·0901	4·33		13·11	·0625	2·25
	16·97	·0847	4·04		12·28	·0580	2·06
	16·12	·0797	3·42		11·05	·0547	1·85
	15·23	·0744	3·03		10·58	·0506	1·59
	14·36	·0696	2·68		9·99	·0460	1·25
	13·58	·0651	2·42		9·33	·0427	1·11
	12·74	·0605	2·06		8·67	·0391	1·02
	12·01	·0566	1·90		8·15	·0368	0·88
	11·28	·0527	1·61				
	10·48	·0485	1·39	60	26·69	0·1509	− 13·30
	9·90	·0455	1·23		25·69	·1432	12·11
	9·24	·0422	1·06		25·44	·1414	11·45
	8·40	·0380	·87		24·41	·1339	10·42
	7·48	·0335	·74		23·38	·1265	9·55
	6·64	·0295	·60		22·14	·1179	8·05
	5·86	·0258	·50		21·21	·1115	7·44
	5·16	·0225	·40		20·10	·1042	6·75
					19·03	·0974	5·87
40	22·66	0·1214	− 7·66		18·01	·0910	4·98
	22·47	·1201	7·26		16·85	·0840	4·49
	21·46	·1132	6·54		15·78	·0775	3·63
	20·41	·1063	5·94		14·85	·0723	3·13
	19·43	·0998	5·20		13·97	·0673	2·87
	18·17	·0920	4·63		13·13	·0627	2·47
	17·22	·0860	4·11		12·31	·0582	2·05
	16·30	·0807	3·64		11·45	·0536	1·76
	15·46	·0758	3·32		10·60	·0492	1·57
	14·57	·0707	2·85		9·54	·0437	1·15
	13·75	·0661	2·50		8·54	·0387	1·02
	13·27	·0634	2·40				

correct temperature. In neither case was any change of temperature perceptible in the water in the flask.

Any error due to diffusion of the solution from the flask into the solvent in the dilution vessel was prevented by running in a weighed amount of solvent before each experiment.

To sum up, therefore, for the dilute solutions of cane sugar, and for those of urea, the heats must be regarded as somewhat more appproximate than those for substances previously investigated with this apparatus. In the case of the calcium chloride solutions and the stronger solutions of cane sugar, however, the accuracy may still be taken as 1 to 2 per cent.

Theoretical Discussion.

(a) **Vapour Pressure and Heat of Dilution.**—The values obtained for the heat of dilution were tested by comparison with the heats calculated from vapour pressure measurements; extensive series of these were available for all the substances investigated, those for cane sugar having been measured by Downes and Perman,[13] for urea in alcohol by Price,[10] and for calcium chloride in alcohol by Miss Hayward and Perman.[11] The method of calculation was that used by Harrison and Perman.[1] The results are given in Table V. It is seen that for urea the agreement is as good as could be expected with such small heats, while for calcium chloride it is exceptionally close. For the cane sugar solutions, however, the agreement between the calculated and observed heats is very poor, the former in every case being considerably greater than the latter. Although small errors in the vapour pressures are sufficient to cause large errors in the calculated heats, the discrepancies here are too great to be ascribed to experimental error, especially as the error is consistently in the same direction. Downes and Perman found the same discrepancies, while Wood[14] calculated a few heats from his vapour pressures, and obtained for concentrations of 60-70 per cent. values from 5 to 14 calories per gram, compared with the present observed values of about 2 calories per gram. That the errors are not due to the use of air-current data, as has been suggested, is shown by the fact that for the other substances the agreement is good, although for them also the air-current method has been used for the vapour pressures; further, the method used by Wood was a static one. Although this method of calculating heats of dilution is too uncertain to enable any definite conclusions to be drawn, it does seem from the present work that there may be some discrepancy in applying Kirchhoff's equation to cane sugar, which does not affect the other substances whose heats have been measured up to the present; the nature of this can only be determined by further investigation.

(b) **Osmotic Pressure and Heat of Dilution.**—For an ideal solution the osmotic pressure is proportional to the absolute temperature; an ideal solution is, however, assumed to have no heat of dilution. For the solutions investigated in the present work, the heat of dilution gives a measure of the departure of the osmotic pressure from the ideal law, and the relation between heat of dilution and osmotic pressure has been shown by Porter[15] to be given by the nearly exact equation :—

$$H_t = sT^2 \cdot \frac{d}{dT}\left(\frac{P}{T}\right).$$

[13] *Trans. Far. Soc.*, **23**, 95, 1927.   [14] *Ibid.*, **11**, 29, 1915.
[15] *Ibid.*, **13**, 131, 1917.

TABLE V.—Comparison of Calculated and Experimental Heats of Dilution.

	Concentration Per Cent.	n/N	Temperature ° C	Calculated Heat.	Observed Heat.
Cane Sugar . . .	20	0·01316	20	0·17	0·08
			40	·19	·13
			60	·22	·15
			80	·24	·17
	30	·02255	20	1·01	0·19
			40	1·15	·26
			60	1·30	·30
			80	1·47	·36
	45	·04305	20	1·41	0·52
			40	1·61	·63
			60	1·82	·74
			80	2·05	·85
	60	·07894	20	1·84	1·40
			40	2·10	1·46
			60	2·38	1·50
			80	2·67	1·55
Urea in alcohol . . .	2	0·01564	30	0·005	0·007 *
			40	·006	·015 *
			50	·029	·026 *
	3	·02371	30	·013	·019 *
			40	·014	·032 *
			50	·037	·045 *
	4	03195	30	·045	·040 *
			40	·063	·059
			50	·113	·073
	5	·04035	30	·053	·071
			40	·088	·094
			50	·133	·115
	6	·04805	30	·095	·115 *
			40	·156	·148
			50	·192	·180
	7	·05771	30	·180	·188 *
			40	·252	·222
			50	·347	·260
Calcium chloride in alcohol	6	0·0205	20	0·39	0·45
			30	·42	·49
			40	·44	·50
			50	·47	·52
			60	·50	·54
	10	·0461	20	1·10	1·20
			30	1·18	1·25
			40	1·26	1·30
			50	1·34	1·32
			60	1·42	1·36
	14	·0675	20	2·29	2·38
			30	2·45	2·56
			40	2·61	2·62
			50	2·78	2·73
			60	2·96	2·80
	18	·0910	20	4·04	4·08
			30	4·32	4·40
			40	4·61	4·53
			50	4·91	4·87
			60	5·22	5·12
	22	·1169	20	6·11	6·00 *
			30	6·53	6·34 *
			40	6·97	7·00
			50	7·42	7·62
			60	7·89	8·12

* Extrapolated Values.

H_i is here the internal heat of dilution, but the error involved in using the heat of dilution obtained by ordinary mixing is slight.

s is the change of volume on adding one gram of the solvent to a large quantity of the solution.

In order to use this equation to determine osmostic pressures over large ranges of temperature and concentration, it is necessary to have a standard set of values obtained experimentally for a range of concentration at one given temperature. This has been done in the present work for cane sugar, using a set of values at 60° C., taken from the work of Morse and of Frazer and Lotz. Since there is no expression for the variation of heat of dilution with temperature, the values of P for any other temperature cannot be obtained by simple integration. Values of

$$H_i/sT^2 \left(= \frac{d}{dT}\left(\frac{P}{T}\right) . \right)$$ were therefore calculated from the experimental

heats, using values of "s" calculated from the densities; values of P/T, and hence of P, at any temperature and concentration were then obtained by graphical integration, using the corresponding standard value of P/T at 60°.

A complete set of these calculated osmotic pressures for concentrations of 25-65 per cent. and temperatures from 0" to 80° is given in Table VI., while in Table VII. a comparison has been made wherever possible with experimentally determined values. The values given in the last column are those calculated by Downes and Perman [13] from their vapour pressure measurements, using the equation of Berkeley and Hartley.

Owing to the difficulties connected with the direct measurement of high osmotic pressures, it is probable that the values calculated from the heat of dilution and a standard set of experimental values are more accurate than those obtained directly. It can be seen that in the present work the agreement between calculated and observed values is fairly good on the whole. It is to be noted that at 0°, at which temperature the heats of dilution were somewhat lower than would be expected, the agreement with the results of Berkeley and Hartley and of Morse is as good as at the other temperatures.

TABLE VI.—Osmotic Pressures of Cane Sugar Calculated from the Heats of Dilution.

Tempera-ture °C.	Osmotic Pressure (in Atmospheres) at Concentration (Per Cent.).								
	25.	30.	35.	40.	45.	50.	55.	60.	65.
0	23·57	30·98	41·51	53·18	68·06	87·69	—	—	—
20	25·04	33·99	44·01	56·29	72·18	92·10	118·32	153·50	206·76
30	25·69	34·87	45·10	57·61	73·87	94·18	120·58	156·76	210·83
40	26·33	35·70	46·16	58·97	75·48	95·19	123·08	160·00	215·06
50	26·92	36·50	47·16	60·21	77·05	98·12	125·53	163·22	219·41
70	28·10	38·00	49·04	62·54	79·93	101·73	130·28	169·64	228·42
80	28·62	38·70	49·92	63·63	81·28	103·46	132·59	172·86	233·04

TABLE VII.—CANE SUGAR.

Comparison of Calculated and Experimental Osmotic Pressures.

Concentration. (Per Cent.).	Temperature. (°C.).	Calculated from Heats.	Morse.[16]	Berkeley and Hartley.[17]	Frazer and Myrick.[18]	Frazer and Lotz.[19]	Downes and Perman.[13] (Calc'd.).
25	0	23·6	24·1	24·0	—	—	—
	20	25·0	25·9	—	—	—	—
	30	25·7	26·5	—	—	—	—
	40	26·3	26·9	—	—	—	—
	50	26·9	27·4	—	—	—	24·6
	70	28·1	27·9	—	—	—	24·7
	80	28·6	28·1	—	—	—	25·1
30	0	31·0	—	31·6	—	—	—
35	0	41·5	—	41·6	—	—	—
40	0	53·2	—	53·6	—	—	—
	30	57·7	—	—	57·4	—	—
45	0	68·1	—	68·8	—	—	—
	30	73·0	—	—	72·8	72·9	—
	40	75·5	—	—	—	—	73·3
50	0	87·7	—	88·0	—	—	—
	30	94·2	—	—	92·6	—	—
55	30	120·6	—	—	120·4	—	—
60	30	156·8	—	—	156·8	157·5	—
65	30	210·8	—	—	207·6	—	—

Summary.

(1) Using the method of Harrison and Perman (*Trans. Far. Soc.*, **23**, 7, 1927) with slight modifications, the heats of dilution were measured of solutions of cane sugar in water, and of urea and calcium chloride in ethyl alcohol, over as wide ranges as possible of concentration and temperature.

Cane sugar gave a series of curves, the four highest of which intersected very nearly at the same point. A few heats were measured at 0° C.; these were considerably lower than those for the other temperatures. All the heats measured were negative.

Urea in alcohol gave very small heats of dilution, all positive. Calcium chloride in alcohol had negative heats of dilution, and provided a series of curves very close together.

(2) Using the Kirchhoff equation, both in its original form and in the modified form due to Porter (*Trans. Far. Soc.*, **13**, 131, 1917), the heats of dilution of the above solutions were calculated from the vapour pressure. Agreement with the observed values was good for urea and calcium chloride, but very poor for cane sugar, the discrepancies being greater than the normal experimental error.

(3) The heats of dilution obtained for cane sugar were used to calculate osmotic pressures by means of an equation deduced by Porter (*loc. cit.*) and a standard set of experimental osmotic pressures. The agreement between the calculated and observed values was good.

[16] *J. Amer. Chem. Soc.*, **48**, 1912.
[18] *J. Amer. Chem. Soc.*, **38**, 1907, 1916.
[17] *Proc. Roy. Soc.*, **92** A, 477, 1916.
[19] *Ibid.*, 2501, 1921.

THE MOLECULAR CONSTITUTION OF THE α SOLID SOLUTIONS OF TIN IN COPPER AND OF THE CORRESPONDING LIQUID SOLUTIONS EXAMINED THERMODYNAMICALLY.

By F. H. Jeffery.

In a previous paper[1] the author developed a method of examining the molecular constitution of liquid and solid solutions of tin in lead. The same method has been used to examine the α phase, and the liquid phase which occurs from 1083° to 800° in the copper tin series of alloys. A diagram was drawn, the concentrations being expressed in weights of tin per cent., from the results given by Raper[2] and by Stockdale.[3] The iso-thermal portion of the solidus at 800° and the liquidus from 800° to 923° were drawn from Raper's results, the portion of the liquidus between 923° and the freezing point of copper 1083° was drawn from the results of Heycock and Neville, there being little danger of error due to the sheath of the resistance pyrometer at these temperatures, the curve obtained was continuous with that from Raper's results. The boundary of the α solid solution phase was drawn from Stockdale's results. The calculations were made using the atomic weights Sn = 119, Cu = 63·6.

The equation $\log (1 - n') - \log (1 - n) = \dfrac{\lambda}{K'\theta} - \dfrac{\lambda}{K'\theta_0}$ has been applied,

n is the molal fraction of tin in the liquid solution and n' is the molal fraction of tin in the solid solution, θ_0 being the freezing point of copper. The equation is applicable to dilute solutions; provided the molecular constitutions be suitably chosen $\log \dfrac{1 - n'}{1 - n}$ must be a linear function of $\dfrac{1}{\theta}$.

The simple assumption that the tin and copper were present in the liquid and solid solutions as monatomic molecules without any compound formation did not satisfy the equation.

When the assumption was made that both liquid and solid solutions were derived from the components Cu_4Sn and monatomic molecules of copper, *i.e.* that all the tin present was dissolved as Cu_4Sn in the copper that remained as solvent, the following results were obtained.

θ	Per Cent. Tin in Liquid.	Per Cent. Tin in Solid.	n	n'	$\log \dfrac{1 - n'}{1 - n}$	$\dfrac{1}{\theta}$
1356	0	0	0 × 10⁻²	0 × 10⁻²	0 × 10⁻²	7·375 × 10⁻⁴
1340	2·5	0·3	1·43	0·17	0·55	7·463
1323	5	0·7	3·07	0·38	1·19	7·559
1303	7·5	1·0	4·98	0·55	1·98	7·675
1283	10	1·5	7·23	0·83	2·90	7·794
1255	12·5	2·4	9·93	1·37	3·94	7·968
1223	15	3·7	13·15	2·19	5·16	8·177
1193	17·5	5·3	17·18	3·29	6·73	8·382
1157	20	7·5	22·30	4·98	8·74	8·643

[1] *Trans. Faraday Soc.*, **26**, 86, 1930.
[2] *J. Inst. Metals*, **38**, 217, 1927.
[3] *Ibid*, **34**, 111, 1925.

If $\log \dfrac{1 - n'}{1 - n}$ be plotted as a function of $\dfrac{1}{\theta}$ it will be found that the points lie sensibly on a straight line through $n = n' = 0$, $\theta = 1356$.

From this it follows that the a solid solution consists of Cu_4Sn dissolved in copper, the molecules of copper being monatomic and that the liquid solution within the range of temperature defined consists of Cu_4Sn dissolved in liquid Cu, the molecules of which are also monatomic.

The great range of concentration within which the equation is applicable is noteworthy : the case of solutions of tin in lead is similar, though there is no evidence of compound formation of tin with solvent lead and the equilibrium diagram for these metals is simple.

The molecular constitution of these solutions of tin in copper is compatible with the complexity of the equilibrium diagram of the copper rich alloys.

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THE MOLECULAR CONSTITUTION OF THE β SOLID SOLUTIONS OF TIN IN COPPER EXAMINED THERMODYNAMICALLY.

By F. H. Jeffery.

In the preceding paper [1] the a phase of the copper tin series was shown to be a solid solution of Cu_4Sn in copper. The β phase on cooling can produce a two-phase system containing the compound Cu_3Sn and also one containing the a phase which therefore involves the compound Cu_4Sn. The following is an attempt to examine the constitution of this β phase thermodynamically.

The diagram of the a, mixed a and β, and β regions was drawn from the results of Raper [2] and of Stockdale ; [3] the a phase boundary from Stockdale's numbers, the 800° and the 520 isothermals and the β phase boundary adjacent to the mixed a and β phase from Raper's numbers. This latter boundary was not drawn as Raper drew it ; the author has drawn a smooth curve from the 800° isothermal to the eutectoid at 520° containing 26·85 per cent. tin. This curve passes close to and between Raper's two points 589° – 588° for 24·8 per cent. tin and 585 – 582° for 25·5 per cent. tin. The curve has a point of inflexion in the neighbourhood of 560° and 26·2 per cent. tin. A point of inflexion on a continuous curve forming the boundary of a single phase is not consistent with a new phase boundary arising from that point ; for such, a discontinuity of the type known as " point saillant " is necessary. This curve has been determined by Raper's numbers, but for the method of using these numbers together with all such consequences as may be implied the author is alone responsible, the value of Raper's results being in nowise affected.

It will be noticed that the boundary separating the a phase region from the mixed a and β region slopes continuously from 13·3 per cent. tin at 800° to 16 per cent. tin at 520° with decreasing temperature, the boundary

[1] *Trans. Faraday Soc.*, **27**, 136, 1931.   [2] *J. Inst. Metals*, **38**, 217, 1927.
[3] *Ibid.*, **34**, 111, 1925.

separating the β phase region from the mixed α and β region also slopes continuously from about 23 per cent. tin to 26·8 per cent. tin. Hence a β alloy at a certain temperature must, when cooled to a slightly lower temperature, produce an α alloy richer in tin than the α alloy corresponding to the initial temperature, and a β alloy also richer in tin than the initial β alloy. One mode of satisfying these conditions would be that β is a solid solution of monatomic tin molecules in monatomic copper molecules, and that α is formed by both copper and tin from β reacting according to the equation

$$4Cu + Sn = Cu_4Sn.$$
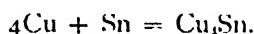
Such a constitution of β is consistent with the various bodies which separate from it on cooling. If this explanation is unique, the thermodynamic consequences must be consistent with the experimentally determined values which give the α and β boundaries.

If n is the molal fraction of tin in the β phase and n' the molal fraction of Cu_4Sn in the α phase, copper being the solvent in each phase,

$$\nu_0 \log (1 - n) + \nu_1 \log n + \nu_0' \log (1 - n') + \nu_1' \log n' = \log K,$$

where $\qquad \nu_0 = -4, \quad \nu_1 = -1, \quad \nu_0' = 0, \quad \nu_1' = 1.$

Hence $\qquad -4 \log (1 - n) - \log n + \log n' = \log K$

also $$\frac{\partial}{\partial \theta} \log K = \frac{-\lambda}{R\theta^2}.$$

For reasons similar to those given in a preceding paper [4] the integration is

$$-4 \log (1 - n) - \log n + \log n' = \frac{\lambda}{R\theta} + \left(\log K_{\theta_1} - \frac{\lambda}{R\theta_1} \right)$$
$$= \frac{\lambda}{R\theta} + \text{constant}$$

provided the solutions involved are sufficiently dilute. Hence if these molecular constitutions of α and β have been correctly chosen

$$-4 \log (1 - n) - \log n + \log n' \text{ must be a linear function of } \frac{1}{\theta}$$

The results shown in Table I. were obtained.

TABLE I.

θ.	Per Cent. Tin in α.	Per Cent. Tin in β.	n'	n	$-4 \log (1-n)$ $-\log n + \log n'$.	$\frac{1}{\theta}$
1063	13·4	23·0	$1·10 \times 10^{-1}$	$1·38 \times 10^{-1}$	$1·598 \times 10^{-1}$	$0·941 \times 10$
1043	13·6	23·1	1·12	1·38	1·690	0·959
1008	14·0	23·2	1·18	1·39	1·879	0·992
968	14·4	23·3	1·23	1·40	2·066	1·033
933	14·8	23·6	1·29	1·42	2·236	1·072
908	15·0	23·9	1·32	1·44	2·310	1·101
888	15·2	24·4	1·34	1·47	2·373	1·126
868	15·4	25·0	1·37	1·51	2·431	1·152

The first five points lie sensibly on the straight line through the second and the fourth. The next three points diverge from this straight line, but in a manner such as might be expected for solutions of increasing concen-

trations beyond the applicability of a thermodynamic equation for dilute solutions.

The foregoing affords evidence that the β solid solutions are monatomic molecules of tin dissolved in monatomic molecules of copper.

Discussion of these Results.

If the author's view as to the boundary of the β phase be correct, the equilibrium diagram for these copper rich alloys becomes simpler than that given by Raper. It seems to the author that a continuous curve can be drawn from the eutectoid on the tin rich side of it to meet the 580° isothermal tangentially at the point corresponding to the composition Cu$_4$Sn, and that such a curve is consistent with Raper's experimentally found points. If this be so the portion of the diagram from the 520° eutectoid along the β boundary to the 800° isothermal and that from this eutectoid along the β boundary to the 580° isothermal do not appear to involve any difficulties as far as the theory of heterogeneous equilibrium is concerned, according to this interpretion the β solid solution would give α and Cu$_4$Sn in the neighbourhood of this eutectoid on the copper and tin rich sides of the eutectoid respectively.

The constitutions of the α and β solid solutions for which evidence has been given in this and the preceding paper are compatible with the difficulties which have been found in the micrographic analysis of certain of these copper rich alloys. Such alloys seem capable of giving rise to metastable systems.

The Goldsmiths' Metallurgical Laboratory,
Cambridge.

REVIEWS OF BOOKS.

Handbuch der Technischen Elektrochemie. Vol. 1 Part 1a. **Die Technische Elektrometallurgie Wasserige Losungen.** By VIKTOR ENGELHARDT (Leipzig : 1931. Akademische Verlagsgesellschaft M.B.H.) 586 pp. Price 56 R.M. bound 58 R.M.).

An historical survey of the growth of industrial electro-chemistry from the middle of the last century enables the assignment of four distinct periods during each of which a marked predominance of a particular phase or type of development is apparent. In the first of these periods industrial electro-chemistry of any magnitude was limited to electro-plating and electro-typing followed by the inception in this country, and its subsequent extension elsewhere, of the electrolytic refining of copper. In the second period, commencing towards the end of the eighties, a beginning was made in the active exploitation of electrolytic processes, and industries which became established on a considerable scale included the winning of aluminium, the alkali metals, magnesium, the separation of the noble metals, electro-galvanising, and, in the general chemical industry, electro-chemical processes became established in the production of alkali, chlorine, bleaching liquor and chlorates. In the third period, beginning in the nineties, electro-thermal processes, which hitherto had scarcely outgrown the experimental stage, advanced to the foreground and became the focus of main interest. This period, extending into the first decade of the present century, saw the establishment of the manufacture of calcium carbide, carborundum,

artificial graphite, electric steel and pig-iron, ferro-alloys, fused silica, nitric acid, and other electric furnace products. In the fourth period, from the second decade of this century to the present time, further electro-chemical advances have predominantly reverted to the field of hydro-metallurgical processes. By means of these developments, a range of metals, notably including iron, are now produced in considerable and rapidly-increasing quantities, of special properties due to a degree of purity unattainable by furnace processes, and with a marked increase of economy in the completeness of recovery from the ores.

A delineation of current developments in industrial electro-chemistry was formerly edited by the author of the present Manual with noteworthy success in a series of *Monographien über angewandte Elektrochemie* (Knapp, Halle) which were commenced in 1902 and extended to a total of 51 volumes. The present Manual, which is composed of a collection of articles or monographs by well-known authorities on each special subject marks the beginning of an ambitious project to bridge the gap of recorded progress between the date of the last of these earlier publications and the present time. It is apparent that this Manual is of special value in that it contains considered expert opinion and information of industrial value derived from a first-hand and intimate practical knowledge of the processes. The first section of 78 pages is devoted to theoretical considerations in an article by H. v. Steinwehr and is followed by an article of 120 pages by the editor and R. Gross on a " Constructive Survey of Electro-chemical and Electro-technical Relations." This deals with the composition, construction, and arrangement of electrodes, cells, and diaphragms and the principles of electric generators, transformers, and rectifiers, and of measuring instruments. The remainder of the volume under the general title " Applied Section " contains a brief introductory chapter by the editor on " Technical Electro-metallurgy of Aqueous Solutions " followed by monographs on " Iron " by W. Pfanhauser, " Manganese " and " Chromium " by E. Liebreich, " Nickel" by V. Hybinette, " Cobalt," " Zinc," and " Cadmium " by G. Eger, " Bismuth " and " Antimony " by W. Schopper, "Tin" by C. L. Mantell, and " Lead " and " Mercury " by W. Schopper. In the article on Zinc, noteworthy descriptions are given of the developments recently made by U. C. Tainton in electrolytic zinc extraction which promise to modify the whole aspect of zinc metallurgy. As a result of a personal visit and close inspection by the author of plants now in operation in the United States, well-illustrated descriptions are given in fuller detail than has so-far been published. In the exploiting of large resources, small matters have not been neglected and in the article on Lead, an account is given of processes in successful operation, also by Tainton, in which lead is deposited electrolytically from solutions from the extraction of residues containing as little as 3·5 grm. lead per litre.

Of amendments which might be suggested, it is noted on page 39 that the term – v at the end of eq. (17) should read + v. In giving the expression for a concentration cell on this page, it appears to be overlooked that in changing from a cell provided with boundary transport, though with diffusion potential eliminated, to one in which, as in the example given, the two solutions are separated by an intermediate amalgam electrode, the expression for the potential,

$$\frac{RT}{F} \ln \frac{C_1}{C_2} \text{ changes to } \frac{2RT}{F} \ln \frac{C_1}{C_2}.$$

In the detailed bibliography of the Tainton process given on page 452, reference might well be made to the earliest publications on this subject in Brit. Pat. 7235 of 1911 and *Trans. Chem. Soc.*, 105, 710, 1914.

J. N. P.

British Chemicals and their Manufacturers, 1931 (London : Association of British Chemical Manufacturers), **Official Directory of the British Chemical Plant Manufacturers' Association,** 1931. (London : The Association.)

These basic guides to British chemical industry may be obtained gratis on application to the secretaries of the respective Associations at their offices, 166 Piccadilly, London, W. 1.

The former (which is printed in English, French, Spanish, Italian, Portuguese and German) contains the directory of members of the Association, and a classified list of British chemicals and their makers, together with a list of proprietary and trade names. The latter gives in addition to the directory of members a classified list of their products.

The Physics and Chemistry of Surfaces. By N. K. ADAM. (Oxford : Clarendon Press, 1930. Pp. x + 332. 45 Figs. Price 17s. 6d.)

Dr. N. K. Adam's book on " The Physics and Chemistry of Surfaces " is based upon his long experience in the study of monomolecular films of spreading oils on the surface of water ; but it is of wider scope than might have been anticipated in view of the highly-specialised reputation of the author. Thus, the work of Hardy on Lubrication, of Palmer and Constable on Surface Catalysis, of Quastel on Catalysis by Bacteria, are discussed almost as fully as the author's own experiments. There is also a chapter on " The size, shape and other properties of organic molecules, deduced from X-ray studies and other sources," and a long chapter on the general properties of solid surfaces. Special interest attaches to the sections in which the physical phenomena which are involved in the industrial processes of flotation, wetting and waterproofing are analysed. This has been done with such exceptional clearness and simplicity as to leave the reader with the feeling that the problems in question have really been solved and not merely discussed. In accordance with the general scheme of the book, the subject of heterogeneous catalysis is discussed broadly, in a chapter on " Solid Surfaces : fine structure, adsorption and catalysis," with reference to the properties of the catalytic surface rather than to the effects which it produces in industrial operations ; but there is a final chapter in which the measurement of surface tension is described in full detail.

The book provides a valuable summary of the author's own work and of the diverse phenomena which can be correlated with it. It has the advantage that no attempt has been made to provide a duplicate of Sugden's book on the " Parachor," Hinshelwood's book on " Chemical Change in Gaseous Systems," or Rideal and Taylor's book on " Catalysis." It is indeed a typical English production, as contrasted with a typical German monograph, since, instead of posing as an encyclopædia, it presents the reader with an interesting narrative, based upon a clearly-defined point of view. The book is therefore one which should be *read* and not merely purchased for occasional reference ; and the reading need not be an arduous task, since the publisher has been generous in the provision of large type and ample margins so that the time required would be less than that for a condensed text-book which could be slipped into the pocket of a diligent student.

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Non-Metallic Inclusions in Iron and Steel. By Dr. Carl Benedicks and Helge Lofquist. (Pp. xi + 311. London: Chapman & Hall, 1930. Price 30s. net.)

Professor Benedicks and his colleague have undertaken a formidable task in giving a complete account of the non-metallic inclusions in iron and steel. Far from being merely descriptive, the attempt has been made to interpret the observations and to construct a picture of the physico-chemical equilibria in each of the systems involved.

The principal non-metallic inclusions are oxides, sulphides, and silicates, but other elements enter into the less common inclusions, and the equilibria between metals and such substances as those named are often of a complex character. It will surprise most metallurgical readers to find how extensive is the literature of the subject, the bibliography occupying nineteen closely printed pages. The question of the formation of inclusions and of their behaviour with changing conditions of temperature and concentration is one of great practical importance, the quality of steel depending in an intimate fashion on the quantity and size of the inclusions. The steel-maker, therefore, needs a knowledge of the relations between molten iron and steel, on the one hand, and the fusible oxide-silicate-sulphide systems on the other if he is to control the quality of his product.

In some instances the authors have had to go somewhat beyond the known facts in constructing probable equilibrium diagrams, but they always give good reasons for their choice, and the presentation of the evidence is so thorough that the careful student finds all the material necessary for an impartial judgment of the merits of any proposed solution.

The volume is profusely illustrated, and all the ordinary inclusions are shown, their characteristics being further represented in tabular form. There is also a full account of the methods of chemical isolation, analysis, and micrographic identification, whilst a later section of the work deals with the crystallisation of ingots and its relation to the distribution of inclusions, a subject on which the authors' views have been lately presented in the form of a contribution to a discussion before the Iron and Steel Institute. The general influence of inclusions on the mechanical properties of steel is more briefly discussed, this section forming the conclusion of an excellent book which will be found of great value by all metallurgists who consider their subject from the point of view of physical chemistry, whilst students of chemistry in general will find an examination of it an interesting revelation of the complexity of an important technical application of the inorganic department of the science.

C. H. D.

A Tribute to Michael Faraday. By Rollo Appleyard. (London: Constable & Co. Ltd, Pp. xiii and 203. Price 7s. 6d. net.)

As the author says in his preface—"The occasion is appropriate for recounting the story of his (Faraday's) parentage, his environment, his mode of thought and operation, his sympathies, his difficulties, his victories, and his passion for truth."

We are taken back to the yeoman stock whence he came; then we read the familiar but ever fascinating tale of the bookbinder's apprentice become laboratory assistant and so follow him through Europe on the grand tour, as part assistant part valet, to the return to his real life in Albemarle Street. The narrative has greatly added interest by reason of the frequent extracts from Faraday's note-books and correspondence.

Those who are led for the first time this year (and they will be many) to know something more of Faraday than his name should turn to this volume. They cannot fail to join in the worldwide tribute to this very human and unassuming man who overcame every disadvantage of upbringing to become, in his own lifetime, the centre and mainspring of the great scientific advance of the early and middle nineteenth century and, for all time, the inspiring genius of many of the essential things of civilisation.

The production of the volume is worthy of its contents ; there are copious and interesting illustrations. This book is a human document which should appeal to every class of reader.

Les Statistiques Quantiques et Leurs Applications. Par PROFESSOR LÉON BRILLOUIN. (Les Presses Universitaires de France, 1930. Two volumes. Pp 404. Price 125 francs.)

The author of these volumes well maintains the reputation which he has earned as a skilful expositor of mathematical and physical theories. The subject of statistical mechanics has assumed an added importance within the last few years owing to the advent of the new statistical theory of Bose and Einstein on the one hand, and that of Fermi-Dirac on the other. These theories have been found to have a wide significance and their importance has ricocheted down the sciences. It is now almost essential for every physicist and most chemists to be acquainted with the new developments.

The first of these volumes is concerned with the development of statistical mechanics and its relation to thermodynamics. The idea of *partition function* (or *Zustandssumme* of Planck) is introduced, and its central role in statistical mechanics is pointed out. From it the mean value of the energy, or indeed of any property, of an assembly, can be calculated without recourse to entropy. A description is given of the recent methods of Darwin and Fowler, in which mean values rather than most probable values are calculated. The question of fluctuations is discussed and Einstein's famous investigation of the fluctuation of radiative energy in an enclosure is reproduced, with adequate reference to the important deductions to be drawn therefrom.

The essential features of the Bose-Einstein and Fermi-Dirac statistics are introduced at an early stage, instead of being added at the end of the book as in many text books on statistical mechanics. This definite orientation of the book towards the new theories makes one of its most appealing features. Further the author illustrates in an interesting and instructive way the characteristic differences between the two newer statistics.

In the second volume numerous applications of the new statistics are given in some detail Pauli and Sommerfeld have shown that the " free " electrons of a metal can be regarded as a good example of a degenerate gas, and consequently the statistics of Fermi-Dirac must be invoked to deal with the theories of electrical and thermal conductivity. The new theory is also capable of reproducing the main features of electron emission. The author gives too a very illuminating account of Bloch's theory of electrical conductivity without an undue amount of mathematics.

The reviewer confidently recommends the work as one of the best elementary treatises on statistical mechanics which has yet been produced.

The Scientific Achievements of Sir Humphry Davy. By J. C. GREGORY, B.Sc., F.I.C. (Oxford University Press, 1930. Pp. vii and 144. Price 6s. net.)

The author approaches his subject from a different angle from that adopted in Thorpe's well-known work. Whilst confining himself in large measure to relating the scientific work of Davy, he shows how that work was aided by the thoughts and the experiments of other workers of the day and how it has affected later theory.

The book is lucidly written and will be readily understood even by those who have little or no knowledge of science. Needless to say it is admirably produced.

A Treatise on Light. By R. A. HOUSTON, M.A., PH.D., D.Sc. Sixth Edition (London : Longmans, Green & Co., Ltd., 1930. Pp. xi + 494 and 340 diagrams. Price 12s. 6d. net.)

The new edition of this useful text-book is in great measure a reprint of the previous edition, but the volume now gives a somewhat more extended treatment of the quantum theory and also refers, *inter alia*, to the Raman Effect.

The Theory and Design of Illuminating Engineering Equipment. By L. B. W. JOLLEY, M.A., M.I.E.E., J. W. WALDRAM, B.Sc., and G. H. WILSON, B.Sc., A.M.I.E.E. (London : Chapman & Hall, 1930. Pp. xxxi + 709 and 555 diagrams. Price 45s. net.)

The authors of this very complete treatise are all members of the staff of the Research Laboratories of the General Electric Co., Ltd., at Wembley, and it follows that no better authorities could be chosen for the presentation of the subject.

The volume is, not unnaturally in these days, very largely concerned with equipment for electric illumination. It will suffice in this notice to mention merely some of the matters which are treated ; *e.g.*, calculation of flux and intensity, reflecting and transmitting media ; light sources ; lighting equipment —types and mechanical design ; reflecting equipment—design ; diffusing and refracting media ; projecting systems ; colour media ; street and studio lighting In addition there are some 50 pages of appendices devoted to tables, regulations and specifications.

The book is well printed and substantially bound and has an adequate index ; an interesting and useful feature is a bird's-eye tabular index which constitutes the end fly-leaf

Heat, Light and Sound. By R. G. SHACKEL, M.A (London : Longmans, Green & Co, Ltd., 1930. Pp. viii + 472. Price 5s. 6d. net.)

A text-book of matriculation standard. That part of the book dealing with Heat and Light (375 pp.) is also issued separately, price 4s. 6d. net.

Intermediate Physics. By R. A HOUSTON, M.A, PH.D., D.Sc. (London : Longmans, Green & Co., Ltd., 1930 Pp. xviii and 638. Price 10s. 6d. net.)

A text-book of Intermediate or First Science standard dealing with Dynamics and the Properties of Matter, Heat, Sound, Light, and Electricity and Magnetism.

THE VIBRATION SPECTRA OF SOME SIMPLE CARBON COMPOUNDS CONTAINING THE CARBON-CHLORINE LINKAGE.

I. RAMAN SPECTRA.

By WILLIAM WEST AND MARIE FARNSWORTH.

The following report records observations on Raman spectra of a number of simple carbon compounds which were made as the initial steps in an investigation involving the examination both of infra-red absorption and of scattered spectra to ascertain what connection might exist between the vibration spectra and the chemical behaviour of substances.

It has become customary of recent years to talk of certain bands in the near infra-red region of the spectrum as associated with the chemical bonds existing in the molecule. Thus, all compounds containing the C-H linkage show infra-red bands corresponding to a frequency of about 3000 cm.$^{-1}$, influenced only to a secondary degree by the nature of the rest of the molecule. Similarly compounds containing the N-H group possess a band at about 3400 cm.$^{-1}$; characteristic frequencies can also be ascribed to the C-O and C-C groups, and since, moreover, in the case of hydrides at least, these frequencies usually occur without great alteration in the corresponding diatomic molecules, as they exist in the discharge tube or in flames, it is reasonable to refer to them as indeed bond frequencies. We should, therefore, be able to obtain an approximate idea of the strength of the binding by assuming these vibrations to be simple harmonic and determining the force constant k from the equation $v = \frac{1}{2\pi} \cdot \sqrt{\frac{k}{\mu}}$, where, for a vibrating system of two masses of masses m_1 and m_2, $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$. It is also known that these frequencies in molecules are susceptible to change when a substitution is made in the rest of the molecule,[1] so that their examination appears to offer a means of ascertaining if any relation exists between the changes in chemical behaviour of a molecular group which take place on varying other parts of the molecule, and the changes in vibration frequency produced by the same variations.

Up till now, the C-H group has been most frequently studied. But whereas this group is not conspicuously reactive in most simple organic compounds and cannot therefore be expected to show very great variation in its behaviour with the nature of the substituent, the C-Cl group, as it exists in open chain saturated and unsaturated compounds, shows large

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[1] See, for example, Ellis, *Physical Rev.*, **33**, 27, 1929.

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and fairly clear-cut differences in its behaviour in the two classes of compounds. In the saturated compounds, like $CH_3 . CH_2Cl$ the Cl has relatively high reactivity, being hydrolysed, for instance, rather readily by dilute alkali; if, however, it is attached to an unsaturated carbon atom, as in $CH_2 : CHCl$, the Cl is much more resistant to hydrolysis than in the former class of compound, and when reaction occurs with hot alcoholic alkali it pursues a different course ; if, as in allyl chloride, $H_2C : CH . CH_2Cl$, the Cl is attached to a saturated C in a molecule which also contains unsaturated C, its behaviour is like that of the saturated compound, its reactivity in certain reactions, in fact, being enhanced. It seemed, therefore, that a study of the vibration spectra of the simpler members of the saturated and unsaturated open chain carbon-chloride compounds might yield relevant information in connection with our problem.

The experimental investigation thus resolved itself, in the main, to the search for a frequency which might be characteristic of the C-Cl linkage and to the investigation of the behaviour of this frequency as changes are made in the rest of the molecule. Ellis [2] in 1926 had already concluded, from an examination of the absorption spectrum of chloroform in the near infrared, that a series of overtones existed, which could be ascribed to the C-Cl linkages, springing from a fundamental of wave-number 595 cm. $^{-1}$. As the solution of such a problem as the existence of fundamental vibrations is pre-eminently a case in which the Raman effect offers easily obtained information, we commenced our work by investigating the Raman spectrum of a number of simple C-Cl compounds, with the result that a characteristic frequency of about 600 cm. $^{-1}$ appeared for each compound. In the course of the work there appeared reports from other investigators, particularly Dadieu and Kohlrausch,[3] which included C-Cl compounds, in which this same frequency appeared, so that it seems quite certain that we can talk of a fundamental C-Cl frequency at about 600 cm. $^{-1}$, in the same sense as we consider the C-H frequency at 3000 cm. $^{-1}$.

It is well known, however, that the Raman effect in itself does not give complete information on the vibrations which a molecule can make, just as the infra-red absorption may be unable to unfold the whole story. As is well known, overtones are very weak in the Raman effect, a circumstance which, of course, facilitates the endeavour to find what vibrations are fundamentals ; but even in the matter of finding fundamental vibrations, the two tools are to be regarded as complementary. Moreover, in seeking for the effect of substituents on the binding forces between two vibrating atoms, an examination of the overtones becomes important. Thus, if we find that the law regulating the frequency of the overtones of a "bond vibration" is approximately that for a diatomic homopolar molecule, we shall be able to find a value for the heat of dissociation of the bond. Since differences in binding strength may be expected to show as differences in the anharmonic character of the vibration, and since considerable differences in the wave lengths of the higher harmonics are produced by relatively slight changes in the value of the anharmonic factor $\omega_0 x$ of the theory of the anharmonic oscillator, the examination of the harmonics seems important in the search for a correlation between vibration spectra and chemical behaviour. Our investigation has therefore been planned to include the examination both of the Raman and infra-red spectra of the compounds selected. The present paper gives the data on the Raman spectra ; the infra-red work is sufficiently far advanced to be used in the discussion of our Raman results, but the

[2] *Physical Rev.*, **28**, 25, 1926.   [3] *Berichte*, **63** II, 251, 1930.

specific presentation of the wave-lengths will be postponed until we are convinced of their adequate precision.

Experimental.

The substances examined in the Raman effect were methyl chloride, CH_3Cl, ethyl chloride, CH_3CH_2Cl, vinyl chloride, $CH_2 : CHCl$, propyl chloride, $CH_3CH_2 . CH_2Cl$, isopropyl chloride, $CH_3 . CHCl . CH_3$, and α-, β-, and γ-chloropropylene, $CHCl : CH . CH_3$, $CH_2 : CCl . CH_3$ and $CH_2 : CH . CH_2Cl$ respectively. All were examined in the liquid condition. Those gaseous at room temperature were obtained from commercial cylinders, and liquids, with the exception of the β-chloropropylene, were bought from commercial houses and purified by fractionation.

Preparation of β-Chloropropylene.

The β-chloropropylene was made, starting with acetone, according to the scheme $CH_3 . CO . CH_3 \xrightarrow{PCl_5} CH_3CCl_2 . CH_3 \xrightarrow[KOH]{alcoholic} CH_2 : CCl . CH_3$. The preparation of the intermediate compound in this scheme offers no special trouble, but an attempt to obtain the unsaturated compound from the dichloro- compound by the text-book method of boiling with an ethyl alcoholic solution of KOH gave a very poor yield. Reboul[4] heated the reaction mixture in a sealed tube, a procedure which seems inconvenient to the amateur organic chemist and which, moreover, entails the probability of the production of allylene. At the suggestion of Professor John J. Ritter, we substituted an amyl alcohol solution of metallic potassium for the alcoholic potash, and found the production of the chloropropylene to proceed smoothly and rapidly by boiling at atmospheric pressure. The procedure is to boil a mixture of the dichlor-compound with amyl alcohol containing the requisite quantity of potassium for the elimination of one atom of chlorine. The boiling flask is provided with a reflux condenser through which flows water at 40°. This effectively condenses the amyl alcohol and unreacted on dichlor-compound, while allowing passage of the chloropropylene vapour (B.P. 33°) as soon as it is formed, preventing thus as far as possible the formation of the triple bond compound. The chloropropylene is condensed in a condenser through which flows a rapid stream of cold water, collected in a receiver immersed in ice, and purified by fractionation in the usual way.

The source of light was a 210 volt Cooper-Hewitt quartz arc; an image of this was thrown by means of a large lantern condenser on the scattering tube, about two inches long, of quartz, and drawn out to a blackened horn. In order to prevent the possible polymerisation of vinyl chloride, the ultra-violet light was screened out by Corning Noviol filter. A spherical mirror was placed behind the mercury lamp so as to reflect the image on the arc, and the scattering tube was provided with a semi-cylindrical aluminium mirror. The scattering tube was placed in a tin box, in which solid carbon dioxide, "Dry Ice," was placed to liquefy the gases. The plane polished front of the scattering tube was protected from the deposition of moisture by slipping over it a blackened glass tube which projected from the tin box. This tube was closed at its outer end by a plane polished window, and the air enclosed was dried by calcium chloride. No moisture condensed on the outer window. The tin box was placed within a larger cardboard box, and the intervening space lagged with cotton wool. In this way it was possible to keep dry ice in the box over night and

[4] *Annales Chim.*, 5, **14**, 464.

TABLE I.

Methyl chloride – liquid.

Raman Line. λ.	ν.	Scattering Line.	Δν.	Intensities.	ρ.
4119	24,271	4047	432	1/2	—
4135	24,177	4078	338	1/2	—
4167	23,991	4047	712	5	—
4201	23,797	4078	718	1	—
4228	23,645	4359	-710	1/2	—
4292	23,293	4359	-358	1	—
4431	22,563	4359	372	1	—
4452	22,456	4359	479	1/2	—
4498	22,226	2359	709	10	9/10
4554	21,953	4359	982	1/2	—
4575	21,852	4359	1083	1/2	—
4596	21,752	4047	2951	6	1/10
4613	21,672	4047	3031	1	—
4634	21,574	4047	3129	1	—
4652	21,490	4359	1445	2	—
5003	19,982	4359	2953	3	1/10
5022	19,907	4359	3028	1	—
5041	19,832	4359	3103	1/2	—

Ethyl chloride – liquid.

Raman Line. λ.	ν.	Scattering Line.	Δν.	Intensities.	ρ.
4157	24,049	4047	654	4	8/10
4188	23,871	4078	644	1/2	—
4210	23,746	4047	957	0	—
4230	23,634	4047	1069	1/2	—
4298	23,260	4359	-325	1	5/10
4312	23,185	4359	-250	1/2	4/10
4407	22,685	4359	250	1/2	—
4422	22,608	4359	327	4	9/10
4487	22,280	4359	655	10	8/10
4550	21,972	4359	963	3	10/6
4571	21,871	4359	1064	2	5/10
*4599d	21,738	4047	2965	8	9/10
4639	21,550	4359	1385	1	invis/vis
4650	21,499	4359	1436	5	10/8
5005d	19,974	4359	2961	5	8/10

Vinyl chloride – liquid.

Raman Line. λ.	ν.	Scattering Line.	Δν.	Intensities.	ρ.
4143	24,130	4047	573	0	—
4151	24,084	4047	619	0	—
4169	23,980	4047	723	1	—
4202	23,792	4078	723	1	—
4224	23,668	4359	-733	1/2	—
4284	23,336	4359	-401	2	7/10
4437	22,531	4359	404	7	8/10
4465	22,390	4359	545	0	—
4477	22,330	4359	605	0	—
4500	22,216	4359	719	4	1/10
4540	22,020	4359	915	2	10/10
4565	21,900	4359	1035	2	10/10
4614	21,667	4047	3036	10	8/10
4635	21,569	4047	3134	10	8/10
4652	21,490	4359	1445	0	—
4662	21,444	4359	1491	0	—
4689	21,321	4359	1614	7	1/10
5019	19,919	4359	3016†	4	8/10
5043	19,824	4359	3111†	4	8/10
5679	17,604	5461	703	4	—

Propyl chloride – liquid.

Raman Line. λ.	ν.	Scattering Line.	Δν.	Intensities.	ρ.
4155	24,055	4047	648	2	—
4170	23,974	4047	729	1	—
4191	23,854	4078	661	0	—
4202	23,792	4078	723	0	—
4224	23,068	4047	1035	0	—
4259	23,473	4078	1042	1	—
4276	23,380	4359	-655	1	—
4297	23,266	4359	-331	2	—
4404	22,700	4359	235	2	1/10
4426	22,603	4359	335	4	7/10
4444	22,496	4359	506	1	10/10
4486	22,285	4359	650	8	6/10
4502	22,206	4359	729	1	10/10
4515	22,142	4359	793	0	invis/vis
4531	22,064	4359	871	1	10/10
4565	21,900	4359	1035	0	9/10
4585	21,804	4047	2899	6	8/10
4595	21,757	4047	2946	10	8/10
4632	21,583	4359	1397	1	2/10
4654	21,481	4359	1454	5	10/7
4987	20,047	4359	2894	6	8/10
5004	19,978	4359	2957	10	8/10

* Diffuse = d.

† The lines 5019 and 5043 seem obviously to correspond to the lines 4614 and 4635; the difference in frequency shifts from the scattering line is nevertheless beyond the error of measurement. Repeated measurements on several plates confirm the wave-lengths as given. The only explanation we can suggest is this; there are two mercury lines very near to 5019 and 5043; they do not show usually on the photographs of the scattered spectra. The modified C-H lines originating from the mercury scattering line 4359 should be a few Å. longer than those mercury lines, falling about 0·1 mm. to the long wave side on the plate. They may overlap the mercury lines and what we actually measure may be the centre of gravity of the mercury and Raman lines, which will be of shorter wave-length than the modified line.

TABLE I. (continued).

Isopropyl chloride.

λ.	ν.	Scattering Line.	Δν.	Intensities.	ρ.
4132	24,195	4078	320	0	—
4151	24,084	4047	619	3	—
4189	23,865	4078	650	2	—
4202	23,792	4047	911	2	—
4244	23,556	4359	-621	1	—
4301	23,244	4047	1459	2	—
4404	22,700	4359	235	0	—
4423	22,603	4359	332	4	10/7
4442	22,506	4359	429	1	—
4479	22,320	4359	615	10	7/10
4535	22,042	4359	890	3	10/5
4552	21,962	4359	973	0	—
4566	21,895	4359	1060	0	—
4580	21,828	4047	2875	10	7/10
4611	21,681	4047	3022	10	10/4
4633	21,578	4359	1357	1	—
4652	21,490	4359	1445	8	10/5
4986	20,051	4359	2884	8	7/10
5016	19,931	4359	3004	8	10/4
5560	17,981	5461	326	1	—
5650	17,694	5461	613	4	—

α-chloropropylene.

λ.	ν.	Scattering Line.	Δν.	Intensities.	ρ.
4139	24,154	4047	549	0	—
4173	23,957	4047	746	1	—
4312	23,185	4359	-250	3	—
4402	22,711	4359	224	2	invis/vis
4439	22,521	4359	414	10	9/10
4468d	22,375	4359	560	8	10/10
4507	22,182	4359	753	10	8/10
4541	22,015	4359	920	1	—
4591d	21,776	4047	2927	10	9/10
4618	21,648	4047	3055	10	9/10
4655	21,476	4359	1459	10	10/7
4694s	21,298	4359	1637	10	7/10
4994	20,018	4359	2917	8	—
5025	19,895	4359	3040	2	—

β-chloropropylene.

λ.	ν.	Scattering Line.	Δν.	Intensities.	ρ.
4140	24,148	4078	367	0	—
4153	24,078	4047	625	3	—
4283	23,342	4359	-407	2	—
4295	23,276	4359	-341	0	—
4316	23,103	4359	-228	2	—
4401	22,716	4359	219	1	—
4425	22,598	4359	337	4	—
4436	22,537	4359	398	4	—
4481	22,310	4359	625	10	—
4526	22,088	4359	847	0	—
4554	21,953	4359	982	3	—
4589	21,785	4047	2918	10	—
4606	21,705	4047	2998	10	—
4632	21,583	4047	3120	8	—
4645	21,523	4359	1412	8	—
4694s	21,298	4359	1637	10	—
4994	20,018	4359	2917	2	—
5013	19,943	4359	2992	1	—

Allyl chloride.

λ.	ν.	Scattering Line.	Δν.	Intensities.	ρ.
4095	24,413	4047	290	1	—
4148	24,101	4047	602	3	—
4172	23,963	4047	740	1	—
4209	23,752	4047	951	0	—
4294	23,282	4047	1421	1	—
4414	22,649	4359	286	1	10/10
4440	22,516	4359	419	5	7/10
4476	22,335	4359	600	7	6/10
4505	22,191	4359	744	10	8/10
4547	21,986	4359	949	5	8/10
4604	21,714	4047	2989	8	9/10
4619	21,644	4047	3059	8	9/10
4653	21,486	4359	1449	8	8/10
4697	21,284	4359	1651	8	7/10
5013	19,943	4359	2992	3	—

maintain the temperature below the boiling-points of methyl, vinyl, and ethyl chlorides, $-23°$, $-18°$, and $+12°$ respectively.

The spectra were photographed by the Hilger constant deviation instrument, D 2/4. Plates were measured by a travelling microscope and wavelengths obtained by use of the Hartmann dispersion formula with the mercury lines as standards.

Most of the compounds were also examined for the state of polarisation of their scattered lines. A double image prism, large enough to cover completely the camera lens of the spectrograph was placed in front of the lens. The relative intensities of the components of the scattered light

whose electric vectors were perpendicular and parallel to the direction of the beam incident on the scattering cell were compared visually, and by means of a simple densitometer, using a thermopile and galvanometer. No great accuracy is claimed for the values of relative densities.

Results.

Table I. contains the wave-lengths of the Raman lines. The figures in the column headed "intensities" are visual estimates of the relative densities of the lines, and ρ is the ratio of the component in the scattered beam whose electric vector is parallel to the direction of the incident beam to that component in the scattered beam whose electric vector is perpendicular to the direction of the incident beam.

Summary of Vibration Frequencies for Liquids.

Proceeding on the basis that the frequency differences between the incident mercury lines and the modified scattered lines represent vibration frequencies in the scattering molecule, we can summarise our results in Table II. which denotes vibration frequencies and corresponding wave lengths, and gives a rough estimate of relative intensities and depolarisation factors. In choosing the value of the vibration frequency from the sometimes a little discordant Raman shifts for a given quantum transition, due attention has been made to include as far as possible only measurements in which the Raman line was clearly visible under the measuring microscope. The intensities are designated as very weak, weak, fairly strong, strong, or very strong. The letter "d" after the value of the frequency denotes that the corresponding Raman line was diffuse, similarly "s" denotes an unusually sharp line.

The results are summarised graphically in Fig. 1, in which the relative heights of the lines denote roughly the relative intensities of the vibrations, the figures below the lines denote the depolarisation factor ρ, and the letters "d" or "s" indicate specially diffuse or sharp lines.

Discussion.

A cursory glance at the frequency diagram of these C-Cl compounds shows an essential similarity in the vibration spectra. All the compounds have one or more strong lines between 2900 and 3100; all with the exception of methyl chloride have one or two strong lines between 1400 and 1650, and methyl chloride shows a weak line in this region; all have a line, usually of moderate intensity, but weak in methyl chloride, between 900 and 1000; all have one or more intense lines between 600 and 750; and all have a line of medium or great intensity between 300 and 400. The lines of the last two groups are the most intense and characteristic features of the spectra of these compounds; they are absent in the spectra of methane, methyl and ethyl alcohols, and in general, compounds of similar complexity to those studied but without the C-Cl linkage, and it seems quite certain that the presence of the Cl is responsible for their existence.

The lines of frequency about 3000 are the well-known lines which appear in all compounds containing carbon and hydrogen, and which are absent from carbon compounds not containing H. The infra-red investigations of Ellis, of Bonino, and numerous others, and the accumulated work of all who have investigated Raman spectra has led to the interpretation of this frequency as due to the vibration of the H with respect to the C. As was

TABLE II.

Frequency (cm.⁻¹).	λ μ.	Intensity.	ρ.	Frequency (cm.⁻¹).	λ μ.	Intensity.	ρ.
Methyl chloride.				*Ethyl chloride.*			
372	26·88	wk.	—	250	40·00	v.wk.	4/10
479	20·88	v.wk.	—	327	30·58	f.st	9/10
710	14·08	v.st.	9/10	654	15·29	v.st.	8/10
982	10·18	v.wk.	—	963	10·38	f.st.	10/6
1083	9·234	v.wk.	—	1064	9·398	wk.	< 1
1445	6·920	wk.	—	1385	7·220	wk.	< 1
2952	3·388	f.st.	1/10	1436	6·964	st.	10/8
3030	3·300	wk.	—	2963d	3·374	st.	8/10
3129	3·196	v.wk.	—				
Vinyl chloride.				*Propyl chloride.*			
402	24·88	v.st,	8/10	235	42·55	wk.	1/10
545	18·35	v.wk.	—	333	30·03	f.st.	7/10
605	16·53	v.wk.	—	506	19·76	wk.	10/10
721	13·87	st.	1/10	652	15·34	v.st.	6/10
915	10·93	wk.	10/10	729	13·72	wk.	10/10
1035	9·662	wk.	10/10	793	12·61	v.wk.	< 1
1445	6·920	v.wk.	< 1	871	11·48	wk.	10/10
1491	6·707	v.wk.	< 1	1034	9·671	v.wk.	9/10
1614	6·192	v.st.	1/10	1397	7·158	wk.	2/10
3036	3·293	v.st.	8/10	1454	6·878	st.	10/7
3134	3·190	v.st.	8/10	2897d	3·452	v.st.	8/10
				2951d	3·389	v.st.	8/10
Isopropyl chloride.				*a-chloropropylene.*			
235	42·55	v.wk.	—	230	43·48	wk.	< 1
330	30·30	f.st.	10/7	414	24·15	v.st.	9/10
429	23·31	wk.	—	560d	17·86	st.	10/10
616	16·23	v.st.	7/10	753	13·28	v.st.	8/10
890	11·24	f.st.	10/5	920	10·87	wk.	—
973	10·28	v.wk.	—	1459	6·854	v.st.	10/7
1060	9·434	v.wk.	—	1637s	6·109	v.st.	7/10
1357	7·369	wk	—	2922d	3·422	v.st.	9/10
1445	6·920	st.	10/5	3055	3·273	v.st.	9/10
2880	3·470	st.	7/10				
3013	3·300	st.	10/4				
β-chloropropylene.				*Allyl chloride.*			
224	44·64	wk.	—	288	34·72	v.wk.	10/10
337	29·67	f.st.	—	419	23·87	f.st.	7/10
398	25·13	f.st.	—	601	16·61	st.	6/10
625	16·00	st.	—	744	13·44	v.st.	8/10
847	11·81	v.wk.	—	949	10·54	f.st.	8/10
982	10·19	f.st.	—	1449	6·901	st.	8/10
1412	7·082	st.	—	1651	6·057	st.	8/10
1637s	6·109	st.	—	2990	3·344	st.	9/10
2918	3·427	st.	—	3059	3·269	st.	9/10
2998	3·336	st.|	—				
3120	3·205	st.	—				
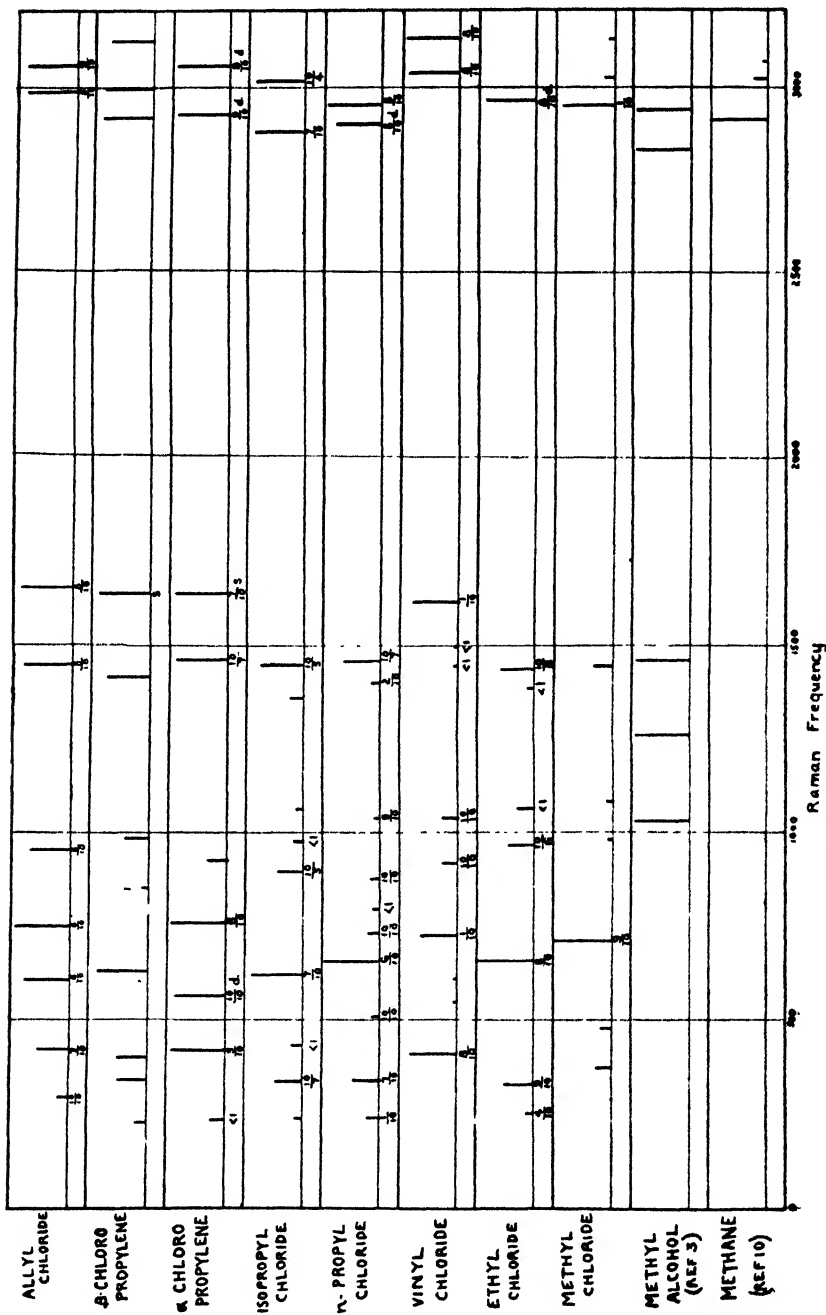
Raman Frequency

FIG. 1.—Raman frequencies of C-Cl compounds,

mentioned in the introduction, the position of this band in the spectrum depends to a comparatively slight degree on the other constituents of the molecule; it is definitely associated with the presence of the C-H group, and may conveniently be termed the C-H bond vibration. In general, any spectral band which we can attribute to the presence of a given group within the molecule, and whose frequency is determined to only a secondary degree by the nature of the other constituents of the molecule, we may associate with a "bond vibration"; the constancy of the position of the band indicates that the period of the dynamic vibration of the two atoms joined by the linkage in question is approximately independent of the rest of the molecule; and indeed, as the following examples show, a bond frequency within a polyatomic molecule has to quite a high degree of approximation, the same frequency as is found to exist in the corresponding diatomic molecule, when it can be studied, in the case of hydrides at least.[5, 6]

TABLE III.—BOND FREQUENCIES.

CH.		NH.		CO.	
In CH diatomic	2800	In NH diatomic	3085	In CO diatomic .	2148
In methane .	3019	In ammonia .	3336	In acetone .	1740
In ethane .	2950	In aniline .	3330	In acetophenone	1660
In pentane .	2930				
In benzene .	3080				

In discussing the concept of the bond frequency, we have to note that its constancy is only relative. It is easy to see on general principles that the constancy will be the greater, the tighter the binding, and the lighter the mass of the vibrating entity. A quantitative discussion of this point for an ideal case of three atoms vibrating in a straight line with simple harmonic motion is given by Dadieu and Kohlrausch. Vibrations of a hydrogen atom with respect to heavier atoms as C, N, O, will thus be the representatives par excellence of bond vibrations. But if, as in the C-Cl linkage, the substituent contributes a substantial share of the total mass of the molecule, the vibration frequency of the linkage will depend more on the masses of the other substituents than that of the C-H linkage. In comparing, therefore, the frequencies associated with the C-Cl linkage in, say, methyl and ethyl chlorides, we shall not be justified in assuming the mass factor determining the vibration to be constant and from variations in the frequency drawing conclusions on the relative magnitudes of the other factor, the restoring force per unit displacement, which we can regard as a measure of the strength of the linkage. We should, however, be able to draw such conclusions from variations in the given frequency as it appears in isomers in which there is a similar distribution of mass, or in compounds which differ from each other only by one having a few more hydrogen atoms than the other. Thus it would seem more valid to consider variations in the frequency of the C-Cl linkage in ethyl and vinyl chlorides, and in the group propyl and isopropyl chlorides, and the chloropropylenes, as indicating differences in the strength of binding within these respective groups.

Assignment of Frequencies.

The Group 2800-3150.—This is the well-known group of lines associated with the presence of C-H groups and attributed to the vibration of the

[5] Mecke, *Trans. Faraday Soc.*, **25**, 938, 1929.
[6] Badger and Mecke, *Z. physik. Chem.*, **B.5**, 344, 1929.

hydrogen atom with respect to carbon. The C-H frequencies can be placed in two groups; one, of the lower frequency, associated with the C-H vibration in a saturated molecule; the other, of higher frequency, with the vibration in a molecule containing doubly-linked carbon atoms. Thus ethyl chloride has a fuzzy Raman line, probably a close doublet, corresponding to a molecular frequency of 2965; vinyl chloride has two sharp lines at 3035 and 3135 respectively. Propyl chloride has two frequencies in the low frequency C-H vibrational region; the chloropropylenes, with one saturated and one unsaturated carbon-carbon linkage, have both types of frequency. This behaviour of open chain compounds containing both saturated and unsaturated linkages is paralleled in those aromatic compounds, like toluene, containing aliphatic side chains. Thus benzene has only C-H vibrations of the unsaturated type, while toluene shows also the lower frequency associated with the C-H linkage in open chain saturated compounds.[7]

The Group 600-750.—There is also no doubt that the lines in this group are due to the presence of the chlorine atom in the molecule. They are present in all Raman spectra of compounds we have examined containing the C-Cl linkage, and are absent from the spectra of compounds of corresponding complexity without chlorine. Moreover, the corresponding frequencies have been found by absorption measurements in all C-Cl compounds. The shift from 710 in methyl chloride to 655 in ethyl chloride is to be attributed to the difference in the mass factors. Again, the presence of an unsaturated carbon-carbon linkage in the molecule causes a shift to higher frequencies, thus from 655 in ethyl chloride to 725 in vinyl. There is a material diminution in frequency in passing from propyl to isopropyl chloride. The single band of the propyl chlorides splits into two sharp bands in the unsaturated compounds, α- and γ-chloropropylenes, one frequency much higher than in the saturated compound, about 750 cm.$^{-1}$, and agreeing generally with the C-Cl frequency in vinyl chloride, and one frequency lower. Apparently it is of no great moment with respect to the values of the frequencies whether the Cl is attached to a double bonded C atom, as in α-chloropropylene, or to a C which is itself saturated but adjacent to a double bonded C atom, as in allyl chloride. (560 and 750 in α-chloropropylene; 600 and 750 in allyl chloride.) In β-chloropropylene only one frequency appeared in this region at 625, close to that at 615 in isopropyl chloride.

The group of lines between 300 and 420 cm^{-1} is also without doubt associated with the presence of chlorine, and is to be attributed to another kind of vibration, perhaps perpendicular to the direction of the bond. This vibration shows great constancy in the saturated compounds, 327 in ethyl, 333 in propyl, 330 in isopropyl chloride. Methyl chloride again has a higher value, at 372 cm.$^{-1}$. In the unsaturated compounds, this line is more intense, and is again shifted considerably to the higher frequencies to a value of about 400 cm.$^{-1}$. All of the compounds except methyl and vinyl also have a feeble line at about 240 cm.$^{-1}$ which is little influenced by saturation or unsaturation.

The assignment of the strong lines at about 1640 cm^{-1} to the C:C linkage seems fairly conclusive. Daure[8] finds a line at 1620 cm.$^{-1}$ in liquid ethylene. Dadieu's and Kohlrausch's spectra of various chlorinated ethylenes, and our own show that the line is present in every unsaturated

[7] Pringsheim and Rosen, *Z. Physik*, **50**, 741, 1928.
[8] *Trans. Faraday Soc.*, **25**, 827, 1929.

compound examined.   The line at 1450, so strong in all the compounds
we have examined except methyl and vinyl chlorides, cannot be attributed
to a specific vibration with the same certainty.   Daure points out its
occurrence in organic compounds containing a simple C-C linkage, with the
implication that it is to be attributed to this vibration.   The line has not
been observed in the Raman spectrum of gaseous methane ;[8, 9] it is strong
in liquid ethane, propane, and in all compounds containing the C-C link-
age.   Our original photographs of the spectrum of methyl chloride did not
show the line ; it appeared, however, faintly on a plate which was given a
very long exposure in order to establish if it were really absent.   It is also
very feeble on the plate for vinyl chloride.   If we considered the Raman
spectra alone, it would seem quite reasonable to attribute the line to the
C-C linkage and to invoke the aid of impurities in methyl and vinyl
chlorides to account for its presence in their spectra.   The shift from 1450
for the C-C linkage to 1640 for C : C would be in accordance with the
effect of the double bond in increasing the C-H and C-Cl frequencies, and
in compounds like the chloropropylenes, containing both kinds of linkages,
both frequencies would appear.   According, however, to Dadieu and
Kohlrausch this frequency is present in methyl alcohol and methylene
chloride, and is absent in certain compounds, as C_2Cl_6, $C_2Cl_4H_2$, in which
the C-C linkage exists, and these authors conclude that the observed fre-
quency at 1450 must be attributed to a vibration of the hydrogen with
respect to the carbon in which the hydrogen moves perpendicularly to the
bonds, a conclusion also reached by Andrews.[10]   This, of course, leaves
unexplained its absence in methane and its weakness in methyl chloride.
The infra-red absorption of the methyl halides shows, however, that a
frequency of about the value 1450 actually exists in these compounds.   The
spectrum of methyl chloride gas, examined at Michigan under the highest
dispersion yet attained in the infra-red, shows a strong band whose centre
is at 1445 cm.$^{-1}$; the structure of the band, moreover, is that theoretically
due to a vibration in which the change in electric moment takes place per-
pendicularly to the axis of symmetry of the molecule.[11]   It must be pointed
out, however, that such " perpendicular vibrations " of Dennison and his
co-workers cannot be interpreted as equivalent to the " transverse vibra-
tions " of Dadieu and Kohlrausch and Andrews, since the infra-red spectrum
of methyl chloride shows that of the group of bands in the neighbourhood
of 3000 cm.$^{-1}$, supposed to originate in the vibration of the H along the
bond, one has the fine structure of a " perpendicular vibration."   It would
be very strange if the force constant for a vibration perpendicular to the
bond were the same as one along the bond.   On the other hand, we find,
in the examination of the infra-red spectrum of vinyl chloride gas, which
will form part of the subject of a later communication, that there is no
indication of a band of appreciable intensity at about 1450 cm^{-1} although
the Raman spectrum does show a very feeble line at 1445 cm.$^{-1}$.   One
might expect the frequency in vinyl chloride to be shifted to higher fre-
quencies, but there is not present in the infra-red absorption of the vapour
a band of any considerable intensity between the region 1445 cm.$^{-1}$ and
1615 cm.$^{-1}$, where there is a strong band agreeing very closely with the
frequency at 1614 cm.$^{-1}$ found by the Raman spectrum for the liquid.
The situation is quite obscure.   The line at 1445 cm.$^{-1}$, which seems
to be due either to a C-C or a C-H vibration, is present, neither in all

[9] Dickinson, Dillon, and Rasetti, *Physical Review*, **34**, 582, 1929.
[10] *Physical Review*, **36**, 544, 1930.
[11] Bennett and Meyer, *Physical Review*, **32**, 888, 1928.

compounds containing a C-C linkage nor a C-H linkage. It is evident that we shall have to learn more about the mechanism of molecular vibrations and absorption and scattering before we can give a satisfactory account of this frequency.

No marked regularity in position or intensity seems to exist in the lines, of medium strength except in methyl chloride, in which they are very weak, between 900 and 1050 cm.$^{-1}$. The Raman lines observed in methyl chloride might not in themselves, on account of the possibility of impurity, be regarded as very certain evidence of the existence of a frequency of this value in a compound not containing the C-C linkage, but all doubt of its appearance in methyl chloride is laid by the observation by Bennett and Meyer of a strong "perpendicular" band in the infra-red, whose maximum is about wave number 1020. The assignment of this Raman frequency to a C-C vibration as has been suggested by Daure, Dadieu and Kohlrausch, and Andrews, is therefore subject to the same uncertainty as the assignment of the strong band at 1450 cm.$^{-1}$.

Polarisation of the Raman Lines.

The discovery reported by Raman in his original communication, and confirmed by every subsequent investigation on the subject, that the lines corresponding to a given transition within the molecule were polarised to the same extent, and that the lines corresponding to different transitions were in different states of polarisation obviously promises to be of great significance in the determination of structure when the phenomenon is completely understood.

Our experiments were made with unpolarised incident light; the state of polarisation of the scattered light is described by the ratio of the component whose electric vector vibrates parallel to the direction of the incident beam to that whose elector vector vibrates perpendicularly to this direction, the so-called depolarisation factor of the theory of optical anisotropy. Various values for this ratio have been given, all using calculations based essentially on classical notions; that is, there is supposed to exist within the molecule an oscillator, actual or virtual, which, in virtue of a very close coupling between itself and the ether, causes, by its own vibration, etherial vibrations producing in their state of polarisation the direction of motion of the oscillator, and which conversely, is acted on by light so as to reproduce in its mechanical motion the direction of vibration of the electric vector in the exciting radiation. The various forms which these theories have taken have been discussed by Cabannes,[12] and we content ourselves here with the statement that the maximum value permitted for the depolarisation factor by any of the classical methods of calculation is 6/7. Cabannes himself reports cases in liquids in which the depolarisation was very nearly 1, and we have found several lines in which the factor is definitely and considerably greater than 1. This is illustrated in Fig. 2, which represents the density curve of the Raman spectrum of ethyl chloride made by means of our rough densitometer; the curves are qualitative only.

The existence of Raman lines in the liquid, in which the component whose electric vector vibrates parallel to the direction of the exciting beam has the greater intensity is very difficult to understand on any theory which presupposes a direct mechanical connection between the radiation and the oscillator. On such a theory it becomes necessary to suppose that the oscillator may be set into vibration in a direction perpendicular to the

[12] *Trans. Faraday Soc.*, **25**, 813. 1929.

vibrations of the electric force in the radiation. The condition of a de-
polarisation factor in excess of unity in liquids seems rather rare; it has
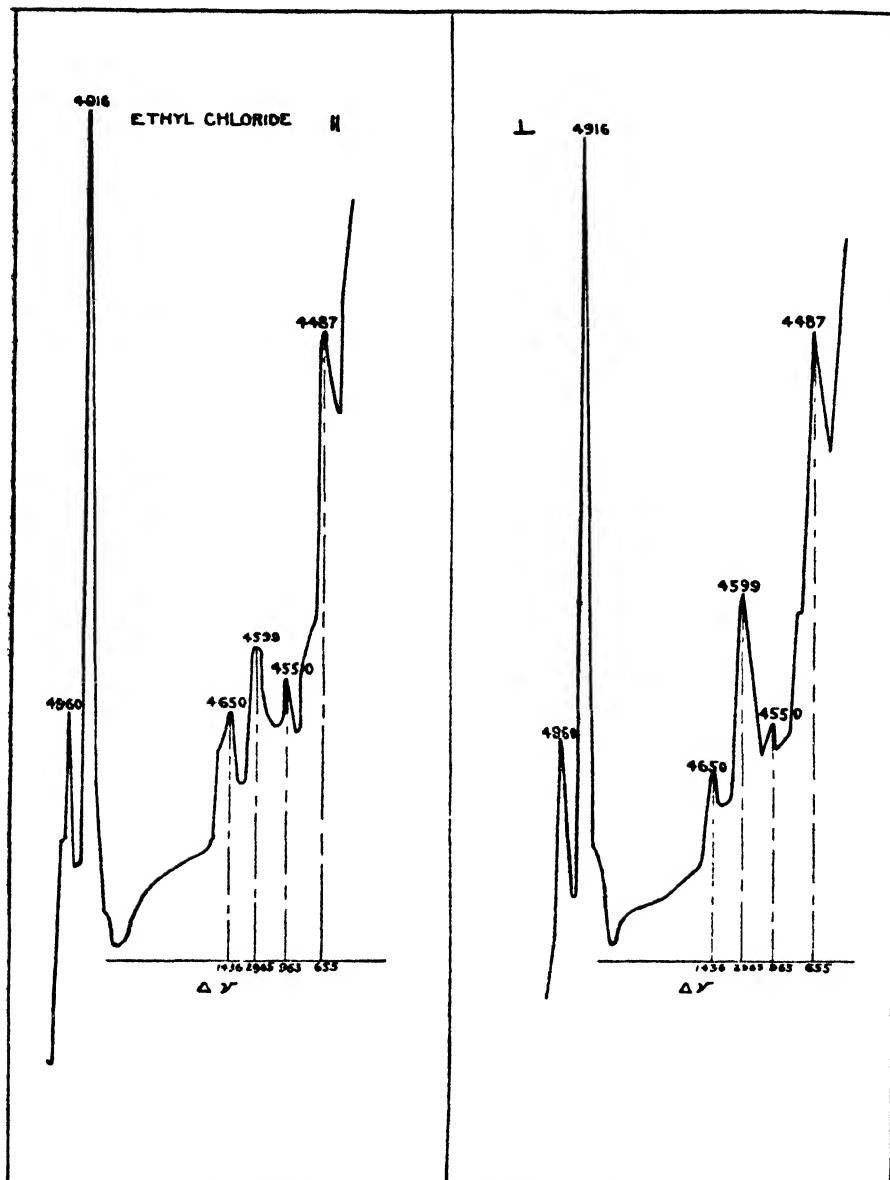
Fɪɢ. 2.—Relative intensities of ǁ and ⊥ components of light scattered by ethyl chloride.

never been observed in unmodified scattering, nor in fluorescence, and so
far as we are aware, the results here reported are the only cases known for
modified scattering in liquids, though Cabannes has found it in the Raman

lines of the crystals, calcite and quartz.* Lack of knowledge of the properties of the energy levels of the compounds here studied makes it impossible for us to attempt the quantum mechanical description of the phenomenon, though it may be mentioned that the theoretical analysis of the polarisation of the Q branch of a vibration-rotation band, given in the Raman effect by a diatomic molecule whose normal state is of the Σ type does not lead to a depolarisation factor in excess of 1.[13]

The empirical facts concerning the state of polarisation of the scattered light are as follows. Lines of a given group in related compounds tend to show the same state of polarisation, though the depolarisation of the lines in the member of lowest molecular weight may be much smaller than in the other members, e.g., C-H vibration in methyl chloride has $\rho = 1/10$; in ethyl and propyl chlorides and the chloropropylenes, $\rho =$ about $8/10$; C:C bond in vinyl chloride has $\rho = 1/10$, in α-chloropropylene, $\rho = 7/10$, and in allyl chloride, $\rho = 8/10$. The tendency towards values of $\rho > 1$ is most pronounced in the groups of lines of frequency about 1400 cm.$^{-1}$ and 900-1000 cm.$^{-1}$. In the infra-red absorption of methyl chloride, bands occur in these regions whose fine structure indicates the type of vibration in which the electric moment vibrates perpendicularly to the axis of symmetry of the molecule. It may be that the abnormal polarisation of the Raman lines corresponding to these frequencies is connected with this type of vibration.

The Group at 3000 cm.$^{-1}$.—In methyl chloride, the most intense line in this group is highly polarised, the depolarisation factor being only about $1/10$. The fainter lines of methyl chloride did not show in our plate in the polarising experiment. In all other cases, there is large depolarisation, of the order $8/10$, except in isopropyl chloride. This is true for saturated and unsaturated compounds alike. When two lines are present in the group, they are polarised to the same extent, except in isopropyl chloride. This compound has two strong Raman lines corresponding to frequencies 2880 and 3013 cm.$^{-1}$; the former is polarised normally as determined by the behaviour of the group of compounds as a whole ($\rho = 7/10$); the latter has $\rho = 10/4$. The lines for propyl chloride are at 2897 and 2951 and have $\rho = 8/10$.

The Group at 1620 cm.$^{-1}$ in Unsaturated Compounds.—In vinyl chloride, this line is highly polarised ($\rho = 1/10$); in α- and γ-chloropropylenes, the lines is largely depolarised ($\rho = 7/10$ and $8/10$ respectively); we lack data on β-chloropropylene.

The Group at 1450 cm.$^{-1}$.—This line, very intense in all compounds except methyl chloride, where its weakness prevented its showing in the polarising photograph, and in vinyl chloride, has in ethyl, propyl, isopropyl chlorides and in α-chloropropylene a depolarisation factor in excess of 1. It is most conspicuously high in isopropyl chloride, where it has a value about 2. In allyl chloride the factor is $8/10$. Vinyl chloride has two feeble lines in this region, in which the depolarisation factor is less than 1.

The Group 900-1000 cm.$^{-1}$.—The lines in this group are highly depolarised. In ethyl and isopropyl chlorides, the factor is greater than 1.

The Group 600-700 cm.$^{-1}$.—These lines have usually depolarisation factors varying from $6/10$ to 1. Vinyl chloride is an exception; its line at 720 cm.$^{-1}$ is highly polarised (ρ about $1/10$).

The Group 300-400 cm.$^{-1}$.—These lines are highly depolarised. Iso-

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* (*Added in proof*) S. Bhagavatan has recently found one line from SO_2 which has a depolarisation factor greater than 1 (*Ind. J. Physics*, **5**, 59, 1930).

[13] Hill and Kemble, *Proc. Nat. Acad. Sci.*, **15**, 391, 1929.

propyl chloride again has $\rho > 1$ (about $10/7$).   The faint lines correspond-
ing to lower frequencies than 300 cm.$^{-1}$, present in some of the compounds,
have depolarisation factors varying from about $1/10$ to 1.

Relation between Vibration Spectra and Chemical Behaviour.

As was mentioned in the introduction, one of our main objects in
carrying out this investigation was to ascertain if any connection could be
found between the vibration spectra of compounds and their chemical
reactivity.   At the outset, however, we are faced with the difficulty that the
concept of chemical reactivity is one to which we cannot give a very definite
quantitative meaning.   In reactions involving more than one molecular
species, the readiness with which reaction occurs is obviously a function of
the properties of the several reacting species; moreover, the only measure
we have of the readiness of reaction, namely the velocity constant of the
reaction, is often a quantity not uniquely determined by the intrinsic
properties of the stoichiometric reactants, but may be profoundly influenced
by such extraneous factors as the presence of catalysts, the physical
properties of solvents, and so on.   The work of Burke and Donnan [14] on
the reactivity of the alkyl iodides shows very clearly the lack of coherence
that exists in the behaviour of these compounds with different reagents.
Thus, in the reaction between the alkyl iodides and silver nitrate, the order
of reactivity is isopropyl $>$ ethyl $>$ propyl $>$ methyl, while in their reaction
with sodium ethoxide to form ethers, the order of reactivity in methyl
$>$ ethyl $>$ propyl $>$ isopropyl.

The vibration spectra give us information on the value of the elastic
force constant associated with the bond, when the two atoms in the linkage
are assumed to vibrate with simple harmonic motion.   We expect then that
there will exist a parallelism between the magnitude of this force constant
and the readiness with which the molecule will enter into a reaction in
which an essential part is the simple breaking of the bond ; a tight binding
will be associated with low reactivity and *vice versa*.   If, on the other hand,
the reaction is determined by such a factor as the formation of an inter-
mediate compound with a distribution of elastic constants very dissimilar
to that existing in the simple compound, a knowledge of the force constants
will not in itself enable us to make predictions about the speed of reaction.
Now the most characteristic difference in behaviour of the saturated and
unsaturated carbon-halogen compounds is the inertness of the latter, when
the halogen atom is directly attached to the unsaturated carbon atom, to
the action of dilute alkali and silver nitrate.   The most characteristic
difference in the vibration spectra of the two classes of compounds is the
shift to higher frequency in the unsaturated compound, and therefore, the
reduced mass not being materially changed, an increase in the force
necessary to produce unit displacement.   It is not unreasonable to associate
the two facts, and we may therefore suppose that the initial stages at least
of the reaction between the alkyl halides and dilute alkali or silver nitrate
are of a rather simple type, in which an essential part is, so to speak, the
stretching of the bond beyond the elastic limit.   The results of Burke and
Donnan on propyl and isopropyl iodides are interesting in this connection.
Silver nitrate reacts with isopropyl iodide in alcoholic solution with im-
mensely greater velocity than with propyl iodide.   We find that for the
corresponding chlorides, the vibration frequency of the C-Cl linkage in the
isopropyl compound is considerably less than in the propyl compound.

[14] *J. Chem. Soc.*, **85**, 555, 1904.

The precise relation between the fundamental frequency and the reactivity of the compounds in this reaction is evidently not simple ; the difference in reaction velocity seems greater than is reasonably to be attributed to the difference in frequency, though it is possible that an examination of the overtones will show a sufficiently marked difference in the anharmonic nature of the C-Cl oscillator in the two compounds to permit the formulation of a more quantitative relation between vibration frequencies and reactivity.

Another significant fact observed by Burke and Donnan in their investigation was the parallelism that existed between the readiness of the alkyl iodides to react with silver nitrates and to undergo photochemical change. They showed that those compounds which most readily react with silver nitrate also most readily give iodine on exposure to sunlight in the presence of air. Now if the photo-chemical reaction of the alkyl iodides is a true unimolecular dissociation, this is precisely the type of reaction whose velocity would be determined by the tightness of the binding of the C-I bond ; one must add the qualification that such a photo-reaction is determined by electronic excitation to a state in which the vibration frequencies may be quite different from those in the normal state. It is true that the photochemical experiments of Burke and Donnan, which were only of a preliminary character, were carried out in the presence of air, and hence may be photochemical oxidations ; Iredale,[15] however, has shown that photochemical decomposition of ethyl iodide takes place in absence of oxygen. We have commenced experiments in this laboratory to examine the photochemical behaviour of these substances in detail.

Summary.

(1) The Raman spectra of unsaturated straight chain compounds in the liquid condition containing the carbon-chlorine linkage have been examined.

(2) One or more strong lines corresponding to molecular frequencies of from about 600-700 cm. $^{-1}$ have been found in all C-Cl compounds, accompanied by a usually less intense line at 300-400 cm. $^{-1}$. These lines are interpreted as representing C-Cl bond frequencies.

(3) The introduction of a double bond in the molecule effects in general, an increase in the value of characteristic frequencies. In compounds containing both saturated and unsatured linkages, both kinds of frequencies occur.

(4) The different characteristic frequencies of related compounds show similar degrees of polarisation. Examples are found of Raman lines in liquids which show depolarisation factors in excess of unity.

(5) Evidence is adduced tending to show that a high value of the frequency of a given linkage, where it can be interpreted as representing a high value of the force constant for the vibration, is associated with comparative inertness of the molecule to reactions in which an important part is simply the breaking of the bond.

[15] *J. Physical Chem.*, 33, 290, 1929.

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THE VISCOSITY OF EMULSIONS. PART II.

By J. O. Sibree.

In Part I. of this Paper,[1] some experiments were described in which the viscosity of certain emulsions was measured, and a number of curves was given, showing the relation between the viscosity and the angular velocity of the outer cylinder of the apparatus. (Part I., Figs. 3, 4, 5 and 6.) These confirm Hatschek's prediction[2] that the viscosity of emulsions varies with the velocity gradient and becomes constant above a critical value.

In addition a curve was given (Part I., Fig. 7M), showing the relation between the viscosity and the concentration of the disperse phase, from which it appears that the formula

$$\eta_s = \eta_0 \frac{1}{1 - \sqrt[3]{\phi}}.$$

does not represent the experimental results, unless a correction is applied to the volume ratio ϕ. This ratio must be multiplied by a factor of about 1·3 (to be called the "volume factor" in the following), if the observed viscosities are to agree with those calculated from the formula. (Part I., Fig. 7N.) The physical meaning of the "volume factor" will be discussed later. The formula quoted above does not contain two factors, which might be expected to play some part in determining the viscosity of the system.

(a) The size of the particles.

(b) The viscosity of the disperse phase.

Even if the size of the particles has no direct effect, it is possible that the volume factor may depend upon it. The simplest test would be the comparison of two or more of the emulsions, each consisting of particles all of one size. Emulsions of this description are difficult to prepare in large quantities. We are, therefore, driven to depend upon determinations and comparisons of the size distribution of the particles. The sedimentation method[3] of determining the size distribution curve was not applicable to these emulsions, since the density of the continuous and disperse phases was equal. Hence, it was decided to make direct measurements of the particle sizes.

Particle Size Distribution.

A sol containing 10 per cent. gelatin was prepared, a small portion of the emulsion added to it while warm, and the whole diluted with 1 per cent. sodium oleate solution so as to bring the gelatin concentration to about 5 per cent. A drop of the mixture was placed between a slide and cover glass and allowed to set, so as to stop Brownian movement; photomicrographs were then taken at suitable magnifications on dry plates or directly on bromide paper. In order to measure the particles with reasonable

[1] J. O. Sibree, *Trans. Farad. Soc.*, 104, 26-36, 1930.

[2] E. Hatschek, *Koll. Z.*, 8, 34, 1911.

[3] For summary, see F. V. U. Hahn, "Dispersoid-Analyse," p. 198, *et seq.* Theodor Steinkopff, Dresden, 1928.

rapidity a series of concentric circles were drawn on transparent material and passed over the photograph. If, for example, the outer circle A had a diameter corresponding to $n\mu$, and the inner circle B a diameter corresponding to $n_1\mu$ then any particles falling between A and B were assumed to have a diameter $\frac{n + n_1}{2}\mu$. As each particle was measured it was marked. Thus the total number of particles of diameter $\frac{n + n_1}{2}\mu$ was obtained, and so on for the other sizes. The percentage number, N, of particles of each size was then calculated, and also the percentage volume V of particles of each size.
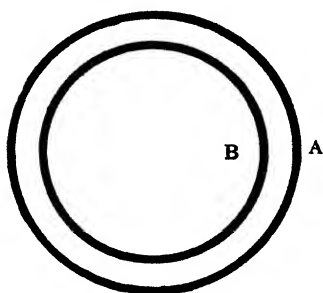
Fig. 1.

The method of plotting the results was to draw $n\mu$ and $n_1\mu$ as abscissæ, and on $(n_1\mu - n\mu)$ as base to draw a rectangle, the area of which represents the percentage number of drops N, which falls between these limits. Thus a series of rectangles is obtained, the total area of which, to a proper scale, is 100. A curve is then drawn through the upper portion of the rectangles, and the curve is smoothed so that the total area bounded by the curve, and the axes of X and Y is 100. The percentage volume V of the particles was also plotted in the same way, since this brings out certain points which are not so clearly seen when N is plotted.

The experimental material of the present paper may be conveniently be divided into two portions (a) that dealing with coarse emulsions, *i.e.*, emulsions containing particles of diameter up to 450 μ; (b) fine emulsions, *i.e.*, emulsions containing particles of diameter up to 20 μ. This arrangement is adopted since the fine emulsions presented particular difficulties of their own.

Coarse Emulsions.

These were prepared as is described in Part I. of this paper, and photo-micrographs were made; since the particles were large, the magnification

TABLE I.—EMULSION B. MAGNIFICATION 51·3.

D (Microns).	N.	N Per Cent.	V Per Cent.
10	349	68·8	0·13
30	46	9·07	0·47
50	22	4·34	1·03
70	38	7·49	4·92
90	22	4·34	6·06
110	5	0·98	2·50
130	8	1·57	6·61
150	5	0·98	6·35
170	2	0·39	3·70
190	0	—	—
210	4	0·79	13·94
230	0	—	—
250	1	0·2	5·88
270	1	0·2	7·40
290	3	0·59	27·50
310	0	—	—
330	1	0·2	13·50

was only 51·3. Table I. gives a typical set of measurements for one of four emulsions, which were as follows :—

(A) Emulsion of viscous paraffin prepared by the capillary tube method.

(B) Emulsion of viscous paraffin prepared by Briggs' method of intermittent shaking.

(C) Emulsion of limpid paraffin prepared by Briggs' method of intermittent shaking.

(D) Emulsion of limpid paraffin prepared by the capillary tube method.
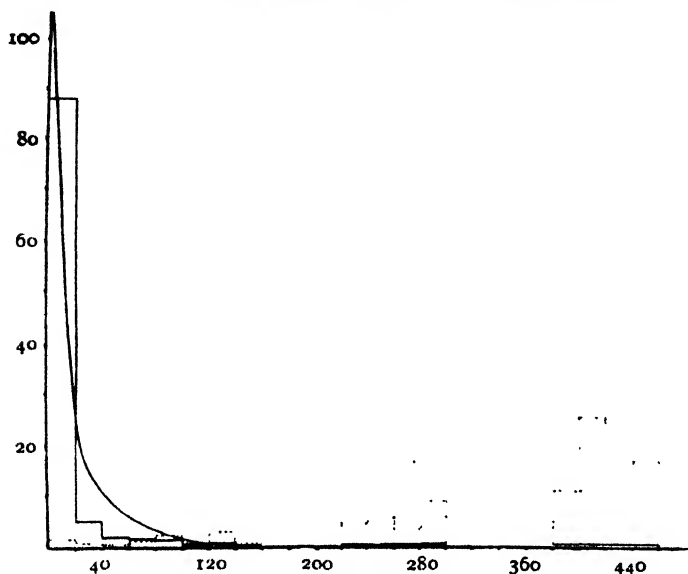
FIG. 2.—Emulsion A. Size and volume distribution of drops. Ord. N per cent. and V per cent. Absc. diameter of drops in microns. Full rectangles N per cent. Dotted rectangles V per cent.

Size Distribution and Volume Distribution.

Figs. 2, 3, 4 and 5, give curves, showing the size distribution of the particles. N per cent. is shown in full lines with a smoothed curve. V per cent. is shown in dotted lines, but does not lend itself to smoothing.

As far as the size distribution is concerned, these show similarities in that the greater number of the particles lie between the limits o and 40μ. There are, however, discontinuities in the curves for A and C,
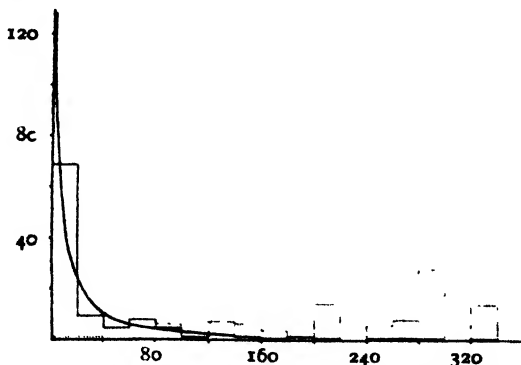
FIG. 3.—Emulsion B. Size and volume distribution of drops. Ord. N per cent. and V per cent. Absc. diameter of drops in microns.
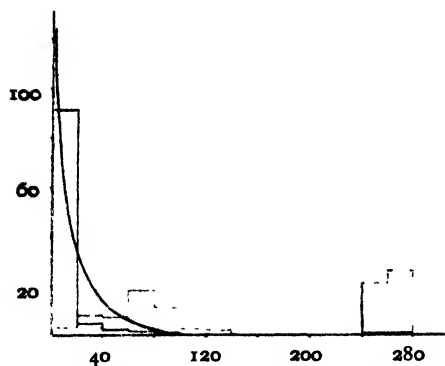
FIG. 4.—Emulsion C. Ord. N per cent. and V per cent. Absc. diameter of drops in microns.
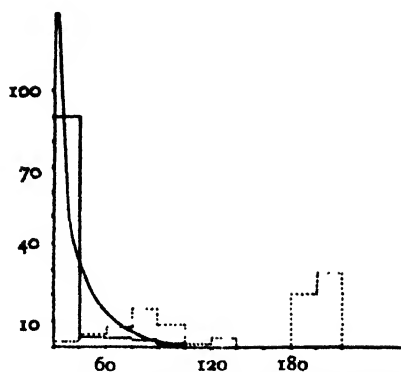
FIG. 5.—Emulsion D. Ord. N per cent. and V per cent. Absc. diameter of drops in microns.
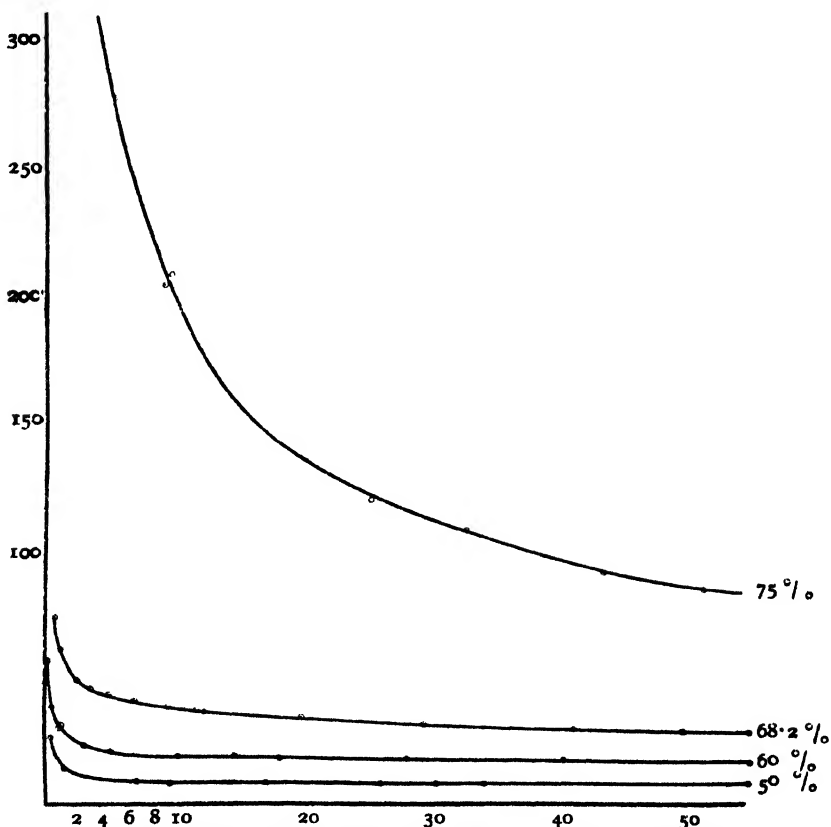
FIG. 6.—Viscosity angular velocity curves. Ord. viscosity relative to continuous phase. Absc. angular velocity in degrees per sec. (Emulsion of limpid paraffin D.) (Table II.)

showing that particles of certain sizes are missing. The volume distribution curves show that the volumes of oil in A and B are very much concentrated in the large particles, while in C and D the volumes are more evenly distributed.

Viscosity Measurements of Coarse Emulsions.

The viscosity of these was measured as described in Part I. of this paper, and the two families of curves in Figs. 6 and 7 were obtained. Identical
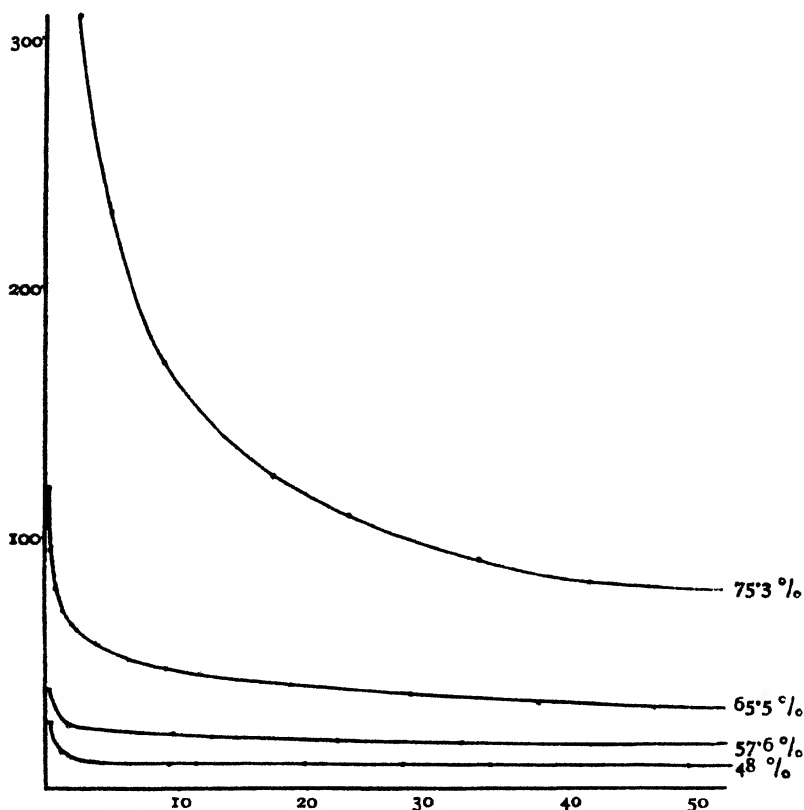
FIG. 7.—Viscosity angular velocity curves. Ord. viscosity relative to continuous phase. Absc. angular velocity in degrees per sec. (Emulsion of viscous paraffin B.) Table II.

results were obtained whether the coarse emulsions were prepared by the capillary tube method, or by Briggs's method of intermittent shaking. The values obtained for the viscosities in the constant region are given in Table II.

ϕ (Calculated) is the volume of disperse phase in unit volume of emulsion calculated from the formula $\phi = \dfrac{(\eta_e - \eta_0)^3}{(\eta_e)^3}$.

$$h = \frac{\phi \ (\text{calculated})}{\phi \ (\text{measured})}.$$

TABLE II.—Coarse Emulsions. Temperature 21·5° C.

Percentage of Oil.	η_s/η_0 Measured.	ϕ (Measured.)	ϕ (Calculated.)	h.	Diameter of Particles (Measured.)
Limpid Paraffin.					
50	7·2	0·5	0·639	1·28	—
60	16·4	·6	·828	1·38	—
68·2	26·4	·682	·890	1·30	220 μ down
75	78	·75	·962	1·28	to 20 μ
Viscous Paraffin.					
48	9·3	0·48	0·711	1·48	—
57·6	18	·576	·786	1·36	—
65·6	33	·656	·912	1·30	340 μ down
75·3	79	·753	·962	1·28	to 20 μ

The concentration viscosity curves for these two emulsions are given in Fig. 8, where

N is the theoretical curve calculated from the formula.

L is the curve for the limpid paraffin emulsion.

M is the curve for the viscous paraffin emulsion.

Fine Emulsions.

As Briggs' and Hatschek's methods do not seem capable of giving emulsions with fine particles, an emulsifier of the beater type was obtained. This is shown in plan and elevation in Fig. 9. A motor, which could be driven at a high speed, is fixed with its axis vertical to a stand. The armature carries a shaft BC and at C there is a propellor, having the tips turned

Fig. 8.—Viscosity concentration curves. Ord. viscosity relative to continuous phase. Absc. concentration as percentage. N curve calculated from formula. M, Table II, emulsion of viscous paraffin. L, Table II, emulsion of limpid paraffin.

down at right angles and dipping into a vessel of about 2 litres capacity. In the interior is a second vessel, FG, perforated with holes, and fixed to

this is a piece of wire gauze, bent in a zig-zag fashion, so that the ground plan is a pointed star. This is shown in plan H. K. When the propellor is revolving in the liquids to be emulsified, they are thrown violently against the projections and forced through the interstices of the gauze, thus disintegrating the disperse phase. By this means, emulsions of viscous and limpid paraffin could be obtained, in which the particles were from 6μ downwards, a large proportion of the particles being in Brownian movement.

Elevation

Plan

Scale of cms.
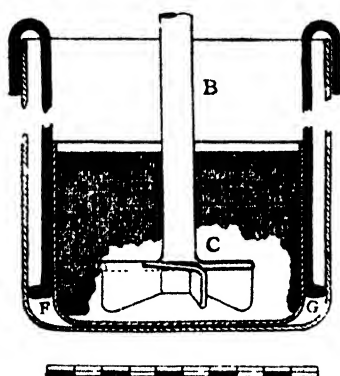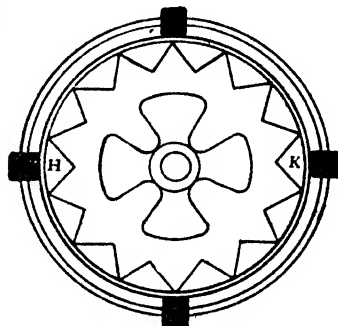
FIG. 5.

These emulsions proved to be remarkably stable and could be kept for several months without any sign of the separation of oil.

Emulsions of limpid paraffin, weighted with bromoform as before, in 1 per cent. sodium oleate solution were prepared of various concentrations, and their viscosities were measured as shown in Table III.*

TABLE III.—FINE EMULSIONS.

Percentage of Oil.	η_e/η_0 (Measured).	ϕ (Measured).	ϕ (Calculated).	h.	Diameter of Particles (Measured).
Limpid Paraffin, weighted with bromoform, to a density equal to that of the continuous phase. Temperature 21·5° C.					
50	8·6	0·5	0·69	1·38	No particles
55	12·8	·55	·784	1·42	above 10μ.
57·6	19·0	·576	·850	1·48	
69·2	190	·092	·984	1·42	
72	900	·720	·997	1·4	
75	Viscosity too high to be measured.				

Air in the Emulsions.

Throughout the range of concentration the viscosity of the fine emulsions was considerably higher than that of the coarse emulsions over the same range, the difference increasing with increasing concentration. The last

* A family of curves obtained similar to those in Figs. 6 and 7.

two viscosities were so unexpectedly high that the presence of air in the emulsions was suspected.   To test this the emulsion containing 69·2 per cent. of limpid paraffin was put in a Winchester Quart bottle, and this was placed on its side so as to present as large a surface of liquid as possible. The bottle was connected to a filter pump, and on reducing the pressure the emulsion gave off bubbles of air which left crater-like marks on the surface.   The filter pump was furnished with a non-return valve, so that it was possible to leave the emulsion under reduced pressure for six days. During the whole of this time air was given off.   At the end of six days the relative viscosity was measured and found to have fallen from 190 to 120.   The presence of air in the emulsions being thus demonstrated, a density determination should give some idea of the quantity present. The density of the last-named emulsion in Table III. was found to be 0·9705 grams per c.c. instead of 1·0004 grams per c.c.

To test this more carefully, a batch of emulsion containing 75 per cent. of limpid paraffin was made up by the capillary tube method, and no bromoform was used to weight the paraffin.   Thus there was no danger of a change in the density of the paraffin during the making of the emulsion. This coarse emulsion was then put into the beater and a viscous emulsion which could hardly be poured was produced.

The measurements of the densities at 21·5° C. were as follows :

Density of 1 per cent. sodium oleate solution   .   1·00036 gms. per c.c.
„   „ limpid paraffin   .   .   .   .   0·80951   „   „   „
„   „ 75 per cent. emulsion   .   .   0·84531   „   „   „
„   „ 75 per cent. emulsion (by calculation) .   0·85722   „   „   „

This gives 1·4 per cent. of air by volume in the emulsion.

It seems surprising that such a small volume of air should give such a great increase in viscosity.   The further question arose whether the coarse emulsion prepared by the capillary tube method contained any air.   To test this a further quantity of emulsion containing 75 per cent. of limpid paraffin was made up as described above by the capillary tube method.   Since this was a coarse emulsion, containing large particles of oil, having a density 15 per cent. below that of the continuous phase, the oil particles rise to the top rather rapidly, making a determination of the density somewhat difficult. The emulsion was therefore put into a separating funnel and samples were taken from the top and the bottom for density determinations.

Density of sample at top   = 0·85843 gms. per c.c.
„   „   „   „ bottom = 0·85814   „   „   „
Average density   = 0·85831   „   „   „
Density of emulsion by calculation = 0·85722   „   „   „

This seems to be as near to an additive result as can be expected, so that this emulsion is obviously free from air.

Attempts were then made to extract the air from the emulsions made in the beater, and the apparatus shown in Fig. 10 was set up.   A is a 10-inch desiccator, BC and B_1C_1, a glass plate lodged at an angle of about 30° to the horizontal inside the desiccator.   The emulsion ran from a separating funnel into a T piece shown end on at E, and in perspective at E_1.   The T piece had its ends closed and numerous holes were blown in it, so that the emulsion could run down the plate in a thin stream.   The whole apparatus was connected to a "Hyvac" pump.   The pressure could be measured by a modified Anschutz gauge F.   In many cases, the emulsion frothed excessively, and to break the froth, an ether tube was fitted.   The

emulsions of limpid paraffin, made in the beater, contained no particles above 10μ in diameter, and according to Stokes' Law, a particle of this size, if unweighted with bromoform, would rise at the rate of about 0·01 mm. per second.   Hence creaming takes place so slowly that it was possible to do away with the use of bromoform to weight the particles.   On the other hand, it was necessary to start with dilute emulsions, so as to make it as easy as possible for the air to be extracted.   A batch of emulsion, containing
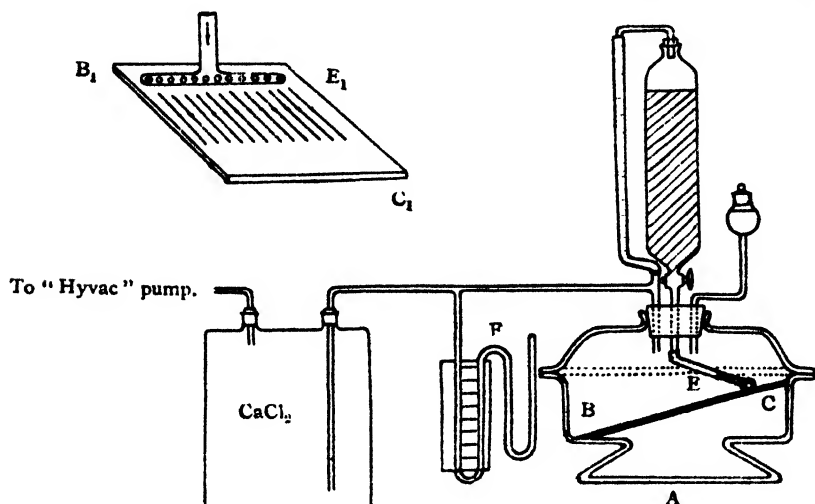
FIG. 10.

30 per cent. of limpid paraffin, was prepared, and this was twice put through the desiccator, care being taken not to go below the vapour pressure of water, so that the water content of the emulsion was not altered.   The emulsion was then put in a separating funnel for about a fortnight to cream. After this period, it separated into two distinct layers, the upper layer containing 69·2 per cent. paraffin, and the lower layer about 2 per cent. paraffin.   The upper layer was used to make viscosity measurements with the result given in Table IV.

TABLE IV.—EMULSION OF LIMPID PARAFFIN, MADE IN BEATER AND PASSED THROUGH DESICCATOR. (TEMPERATURE 21·5° C.).

Percentage of Oil.	η_s/η_0 (Measured).	ϕ (Measured).	ϕ (Calculated).	h.	Diameter of Particles (Measured).
48·4	7·7	0·484	0·659	1·36	No
50·0	8·2	·500	·677	1·35	particles
55·0	12·8	·550	·784	1·42	larger
56·5	14·2	·565	·803	1·42	than 10μ.
58·1	16·7	·581	·831	1·43	
60·0	17·8	·600	·841	1·40	
64·2	46·5	·642	·937	1·46	
69·2	120	·692	·975	1·41	

If the concentration-viscosity curve is plotted from these results, it will be seen that the viscosities are all higher than those for coarse emulsions of

limpid paraffin of similar concentrations. On putting a sample of the 69·2 per cent. emulsion in a Winchester quart bottle, as previously described, and reducing the pressure under the filter pump, air still came off in small quantities for some days.
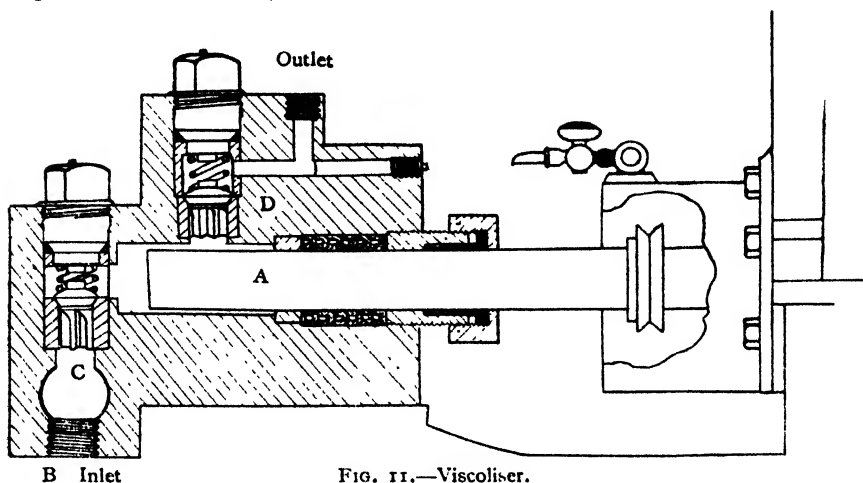
Fig. 11.—Viscoliser.

It therefore appears that it is not possible to remove air completely by a reduction in pressure, and it was feared that continually putting the emulsion through the disiccator would reduce the water content of the emulsion. In this way, the concentration of sodium oleate in the continuous phase would be increased and finally an emulsion of a different character would result. Attempts were therefore made to homogenise a coarse emulsion by some method which avoids the introduction of air. A technical homogeniser, called the "Viscoliser" was employed ; the author is greatly indebted to Dr. Wm. Clayton for the use of his laboratory "Viscoliser" and to his assistants, Miss G. Gell and Mr. G. R. Barnes, for making up the emulsions. The essential details of the apparatus will be gathered from the diagram, Fig. 11.

A is a reciprocating plunger pump and when this moves from left to right, the coarse emulsion is drawn in at the inlet B, the reduction in pressure being sufficient to raise the valve C. When A moves from right to left, C closes and the emulsion is forced past the "homogenising" valve D. This is a conical valve of hard alloy steel, very carefully ground and kept closed by a spring until the pressure rises to about 2000 lbs. per sq. inch. When the pressure is at this value, the valve is forced open very slightly and the emulsion passes through the narrow space, thus subdividing the globules of oil and giving an emulsion with remarkably fine particles.

Fig. 12.—Emulsion of viscous paraffin made in viscoliser. Size and volume distribution of drops. Ord. N per cent. and V per cent. Absc. diameter of drops in microns. Full rectangles N per cent. Dotted rectangles V per cent.

In order to give continuity of flow, the apparatus has 3 pumps working from cams, set at 120° to each other. To cope with the very high pressure used in the process, the cylinder block shown in the diagram is cut from a solid block of alloy steel and the inlet and outlet ports, the valve chambers and plunger chambers are all bored out of the solid block.

It will be seen from the action of the machine that no air is forced into the fine emulsion unless it is already present in the coarse emulsion, and all the experiments point to the fact that the emulsions made in the viscoliser are free from air.

Photomicrographs were taken of the emulsions prepared in this way, and Table V. gives the size distribution of the particles for the emulsion of viscous paraffin. From this Table, it will be seen that there were no particles above 8μ in diameter and that 90 per cent. of the particles were below 2μ in diameter. Fig. 12 shows the size and volume distribution of the particles diagrammatically.

In the emulsion of limpid paraffin, the particles were so small that it was not possible to obtain the size distribution. The photographs, of which a large number were taken, showed no particles

FIG. 13.—Viscosity concentration curves. Ord. viscosity relative to continuous phase. Abscissæ concentration as percentage. N, curve calculated from formula. M, limpid paraffin. L, viscous paraffin, Table VI.

larger than 2μ, and there were only a few as large as this. The viscosities of these emulsions were measured, as described in Part I., and families of curves similar to those in the case of the coarse emulsions were obtained. Table VI. gives the details of the viscosity measurements.

In spite of the extreme difference in particle size, the viscosity of these fine emulsions at the lower concentrations is not very different from that of the coarse emulsions.

This agreement appeared to be accounted for by the absence of air, which was confirmed by putting one of the emulsions under vacuum for 3 to 4 hours, when no liberation of air could be observed. It is, however, by no means easy to account for the enormous effect of comparatively small amounts of air, such as are found in the emulsions made in the beater. No

FIG. 14.—Emulsion of viscous paraffin made in Hurrell mill. Size and volume distribution of drops. Ord. N per cent. and V per cent. Absc. diameter of drops in microns. Full rectangles N per cent. Dotted rectangles V per cent.
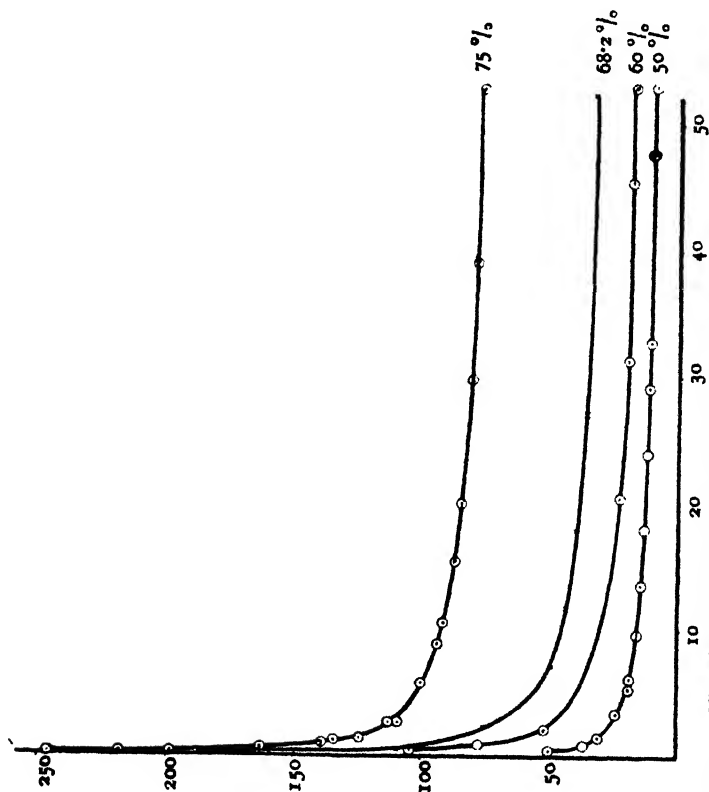
FIG. 15.—Viscosity angular-velocity curves. Ord. viscosity relative to continuous phase. Absc., angular velocity in degrees per sec. *See* Table VIII.

quantitative agreement with the observed high viscosity of an emulsion, containing about 1·5 per cent. air, can be obtained either by assuming that the air increases the volume of the disperse phase, or by considering the continuous phase as an emulsion of air in the soap solution. Fig. 13 gives the viscosity-concentration curves.

By either method of treatment, the amount of air is quite inadequate to account for the observed results and this point must be left for further investigation.

Finally, a fine emulsion of viscous-paraffin in 1 per cent. sodium oleate solution was obtained by means of a Hurrell mill.[4] This mill consists of a casing in which a rotor composed of two discs shaped in section like a truncated cone revolves in close proximity to a similarly shaped stator ring. Both surfaces are perfectly smooth, and the rotor, which is accurately balanced revolves at a speed from 3000 to 8000 r.p.m. The space between the periphery of the rotor and the stator ring may be adjusted from 16/1000ths of an inch upwards.

FIG. 16.—Viscosity concentration curves. Ord. viscosity relative to continuous phase. Absc. concentration as percentage. N curve calculated from formula. M curve from Table VIII.

The materials to be emulsified are fed into the mill at the axis of the discs forming the rotor, and are thrown out by centrifugal force to the periphery, where disintegration is effected by the shearing action in the narrow gap between the edge of the rotor and the stator ring. This emulsion was put under vacuum for 3 to 4 hours and if any air was present, it was only a small quantity.

The size and volume distribution of the particles is given in Table VII. It will be seen that the size distribution is rather different from that obtained in the viscoliser, but that 80 per cent. of the particles are below 4μ in diameter. (See Fig. 14.)

A family of curves giving the relation between the viscosity and the angular velocity of the outer cylinder, is shown in Fig. 15, while Fig. 16 gives the viscosity-concentration curve.

Again, in spite of the extreme difference in particle size, the viscosity of this emulsion is not very different from that of the coarse emulsions throughout the whole range of concentrations.

TABLE V.—SIZE DISTRIBUTION OF PARTICLES IN AN EMULSION OF VISCOUS PARAFFIN IN 1 PER CENT. SODIUM OLEATE SOLUTION. MADE IN THE VISCOLISER. (MAGNIFICATION 515.)

D (Microns).	N.	N Per Cent.	V Per Cent.
0·486	1476	75·5	3·3
1·46	365	18·7	22·2
2·43	90	4·6	25·1
3·40	14	0·7	10·5
4·37	7	0·4	12·7
5·34	3	0·2	11·6
6·31	0	0	0
7·28	1	0·1	14·7

[4] For description, see L. Carpenter, "Mechanical Mixing Machinery," p. 63 *et seq.* E. Benn, London.

TABLE VI.—Emulsion in 1 Per Cent. Sodium Oleate Solution. Made in Viscoliser. (Temperature 21·5° C.)

Percentage of Oil	η_e/η_0 (Measured).	ϕ (Measured).	ϕ (Calculated).	h.	Diameter of Particles (Measured).
Viscous Paraffin.					
51·8	7·62	0·518	0·656	1·27	None
54·6	11·3	·546	·756	1·38	greater
58·9	14·6	·589	·808	1·37	than 8μ.
64·8	21·8	·648	·869	1·34	
71·3	46·0	·713	·936	1·31	
74·8	140·5	·748	·979	1·31	
78·4	500	·784	·994	1·27	
Limpid Paraffin.					
45·1	5·0	0·451	0·512	1·14	None
51·7	10·1	·517	·731	1·41	greater
56·2	14·7	·562	·809	1·44	than 2μ.
66·2	38·0	·662	·923	1·39	
71·0	97·5	·710	·969	1·36	
74·3	280	·743	·989	1·33	

TABLE VII.—Size Distribution of Particles in an Emulsion of Viscous Paraffin in 1 Per Cent. Sodium Oleate Solution. Made in Hurrell Mill. (Magnification 710.)

D (Microns).	N.	N Per Cent.	V Per Cent.
0·37	4	0·33	0
1·07	227	18·7	0·82
1·78	325	26·9	2·01
2·50	196	16·1	3·52
3·21	166	13·7	6·19
3·93	104	8·7	7·23
4·64	71	5·8	8·03
5·37	42	3·5	7·45
6·07	32	2·6	8·10
6·78	13	1·1	4·54
7·50	10	0·8	4·83
8·21	6	0·5	4·43
8·92	6	0·5	5·28
9·64	4	0·3	4·01
10·35	2	0·2	2·56
11·07	3	0·2	5·46
11·84	1	0·1	2·90
12·50	0	0	0
13·21	0	0	0
13·93	1	0·1	3·09
14·64	1	0·1	3·47
15·33	1	0·1	4·05
16·07	0	0	0
16·78	1	0·1	5·4
17·50	0	0	0
18·21	1	0·1	6·81

TABLE VIII.—Emulsion of Viscous Paraffin in 1 Per Cent. Sodium Oleate Solution. Made in Hurrell Mill. (Temperature 21·5° C.)

Percentage of Oil.	η_e/η_0 (Measured).	ϕ (Measured).	ϕ (Calculated).	h.	Diameter of Particles (Measured).
50	9·9	0·50	0·727	1·45	None
60	18·3	·60	·844	1·40	greater
68·2	32·4	·682	·910	1·33	than 19μ.
75	79	·75	·963	1·28	

Discussion of Results.

It has already been pointed out that the two assumptions on which Hatschek's deduction is based are confirmed by the present investigation : the viscosity of emulsions of the same pair of phases is independent of the particle size, or size distribution within very wide limits, and the viscosities of emulsions having the same continuous phase and different disperse phases, is almost independent of the viscosity of the latter. The investigation also proves that the viscosity of emulsions, like that of suspensions of rigid particles and of many lyophilic sols, decreases with increasing velocity gradient and becomes independent of it beyond a certain critical value.

These constant viscosities are comparable and have been used for testing Hatschek's formula connecting viscosity with concentration. As the figures in Tables II., VI. and VIII. show, the formula applies provided the volume of disperse phase is multiplied by a volume factor which for all the emulsions examined is about 1·3, but varies slightly from one emulsion to another, and for any one emulsion varies slightly with the concentration.

The agreement between the formula, with the volume corrected in this way, and the experimental results can hardly be accidental, and the question arises as to what is the physical meaning of the volume factor. Its absolute value makes it impossible to account for the extra volume by assuming merely an adsorption layer, even several molecules thick : the liquid must be affected " hydrodynamically " to a considerable distance from the interface and whatever adsorption layer is formed on the latter. There is, of course, a considerable volume of evidence of such layers of anomalous liquid at interfaces, such as the thixotropic bentonite suspensions (E. A. Hauser),[5] and the great differences in the sedimentation volume of inert powders in various pure liquids (W. Haller).[6] The feature most difficult to explain is, however, that the volume factor is approximately the same for all the particle sizes or size distributions and therefore is not a function of the size of the interface. While emulsions with the same particle size distribution must have specific interfaces (i.e. area of interface per unit volume of system) approximately equal, the difference in specific interface between the extreme types described in the present paper must be enormous.

The fact that the volume factor is not constant for any one emulsion has already been mentioned, but it is not difficult to see the reasons of this variation. With different concentrations of disperse phase the amounts of emulsifier adsorbed from the continuous phase must vary, and, while it is at present idle to speculate how this affects the volume of anomalous liquid, it is obvious that the concentration of soap in the continuous phase, and therefore its viscosity, must vary with the percentage of disperse phase. As this

[5] E. A. Hauser, Koll.-Z., 48, 57, 1929.   [6] W. Haller, ibid., 46, 366, 1928.

viscosity is assumed constant in the formula it is quite natural that the volume factor varies, and probable that it does so in a complicated manner, which for the present is not amenable to analysis.

Finally, it must be pointed out that the continuous phase in all the emulsions investigated has been the same, *viz.*, a 1 per cent. solution of sodium oleate. It is at least possible that the value of the volume factor may be specific for a given emulsifier and concentration. The author proposes to test this assumption by investigating oil-in-water emulsions with emusifying agents other than soap and water-in-oil emulsions.

In conclusion, my thanks are due to Mr. Hatschek for suggesting this investigation, and for the interest he has taken in it during the progress of the work.

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THE IGNITION OF DRIED MIXTURES OF CARBON MONOXIDE ON SILICA.

BY V. E. COSSLETT AND W. E. GARNER.

It is a general property of surfaces that they lower the ignition temperature of combustible gases. This is due to the occurrence of combustion in the layers of gas adsorbed on the surface, at temperatures which are below the ignition temperature of the gaseous phase. The manner in which the heterogeneous reaction is transmuted into flame in the gaseous phase has been the subject of many investigations in recent years, but the relative parts played by (*a*) the rise in temperature of the surface, and (*b*) reaction chains are still far from clear.

There must be an appreciable rise in temperature of the surface layers on a silica surface, because the reactions occurring in flames are strongly exothermic and also fused silica is a bad conductor of heat. This is of importance since the study of flames has shown that the temperature of the combustible gas is a vital factor in flame propagation. The effect of temperature of the combustible gases on the initiation of flame is evident from the work of Dixon and Crofts,[1] who showed that flame might be initiated in the gaseous phase by adiabatic compression. In these experiments, the energy available is in the first place kinetic, and this is absorbed by the gas so as to raise its temperature. It was found that if energy in excess of a certain critical value be supplied to the gas mixture, it burst into flame. Thus, flame can be initiated by the application of kinetic energy, but only if a sufficiently high temperature be produced in the gaseous phase.

Experiments on the ignition of gases by the electric spark also bear on this point. A quantity of energy greater than a certain minimum value must be supplied before flame can be propagated. It would appear, therefore, that for a flame to be stable, it must be backed by gases whose average

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[1] *J. Chem. Soc.*, **105**, 2036, 1914.

temperature exceeds a certain value. This temperature, called the ignition temperature, is not, however, a constant, but varies with the experimental conditions.

Haber, Farkas, and Goldfinger,[2] have shown that it is possible to start a flame in hydrogen and oxygen mixtures by introducing hydrogen and oxygen atoms. The reaction chains started by this means do not, however, give rise to flame unless the average gas temperature is above 400° C.

Reaction chains started by adiabatic compression, an electric spark, or by the introduction of atoms or active molecules do not give rise to flame in combustible gases until their energy content is raised above a critical value. Reaction chains are extinguished if started in gases lacking this energy. The length of the chain, which is partly a reaction and partly an energy chain, thus depends on the temperature.

The same argument must apply to the chains initiated by solid surfaces. These chains will penetrate into the gas phase and will become extinguished, unless the temperature of the gas is above a critical value. One of the functions of the surface in producing flame is to raise the temperature to this value.

The stationary reaction, which occurs at surfaces at temperatures below those of ignition, must consist of the heterogeneous reaction together with a homogeneous reaction in the gases adjacent to the walls. The velocity of such a reaction is divisible into two parts. The first, due to the heterogeneous reaction and the chains initiated by the surface, will be given by

$$r = A \cdot X \cdot n \quad . \quad . \quad . \quad . \quad (1)$$

where A is the area of the surface, X the number of molecules reacting per sq. cm., and n the average length of chain. The second part is caused by the thermal activation of the combustible gas which no doubt occurs, as was shown by Dixon and Crofts' experiments. This is given as the second term in equation 1a,

$$r = A \cdot X \cdot n_1 + \int_0^d k \cdot fc \cdot n_2 \cdot e^{-q/RT} A \cdot dx \quad . \quad . \quad (1a)$$

where n_2 is the chain length, q the critical increment of the activation mechanism, and d the distance to which the chains extend into the gaseous phase.

Equation (1a) has been employed in the following investigation to interpret the results of work on the ignition pressure and the rate of the stationary reaction of carbon monoxide and oxygen mixtures.

Reaction Chains in the Carbon Monoxide Flame.

The nature of the links in the reaction chain in the carbon monoxide flame can only be guessed at. There are, however, certain considerations of a general nature which make it possible to suggest probable steps for the reactions which occur. Certain types of reaction such as, $A + B \rightarrow AB$, are improbable on account of the difficulty of the distribution among the various quantised states of AB of the energy set free by the change.[3] Reactions of the type, $A + BC \rightarrow AB + C$, are much more probable, and even trimolecular reactions occur more readily than $A + B \rightarrow AB$. The latter only occurs to an appreciable extent if the reaction is accompanied by the emission of radiation, which gives a continuous band in the spectrum.

[2] *Naturwiss.*, **17**, 674, 1930.
[3] *Cf.* Beutler and Rabinowitsch, *Z. physik. Chem.*, **8B**, 231, 403, 1930.

In the initiation of reaction chains, the most probable initial activation process is that which requires the least energy. The lowest activation level of O_2 is 37 K. cal., and that of CO is 138 K cal.[4] The activation of oxygen is thus the most probable of the two modes of activation in the carbon monoxide flame.

The most probable reaction chain is, therefore,

$$I. \quad O_2 + M \rightarrow O_2^* + M - 37 \text{ K. Cal.}$$
$$II. \quad O_2^* + CO \rightarrow CO_2 + O + 39 \text{ K. Cal.}$$
and
$$III. \quad O + O_2 + CO \rightarrow CO_2 + O_2^* + 97 \text{ K. Cal.}$$
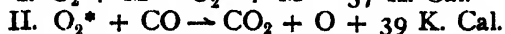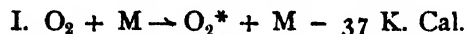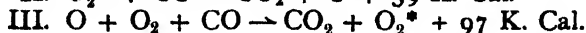
The trimolecular collision, IV., $O_2^* + 2CO \rightarrow 2CO_2$, is less probable than II., since the frequency of collision is small, but since the probability of reaction on collision in II. is unknown, the choice between these two possibilities is somewhat arbitrary.

The processes, $O + O_2 \rightarrow O_3$, $O + O \rightarrow O_2$, are improbable unless they occur on the walls of the containing vessel. $O + O_2 + M \rightarrow O_3 + M$ is, however, possible, and may complicate the nature of the chain mechanism if it occurs.

The chain given above can be most readily broken by deactivation of O_2^*, the recombination of oxygen atoms being less probable. The chains will be broken both in the gas phase and on the walls of the containing vessel.

The parts played by oxygen and carbon monoxide in the above chain mechanism are very different. The chains are initiated by the activation of oxygen, and thus the number of chains started in unit volume will depend on the oxygen concentration. On the other hand, the chain length will be increased to a greater extent by an increase in the carbon monoxide concentration than by the same increase in the concentration of oxygen. (See II. and III)

Some unpublished work by Mr. F. E. Harvey on the extinction of flames as they approach cold solid surfaces shows that in the presence of excess of carbon monoxide the flame burns nearly to the wall before being extinguished, whereas when there is no excess of one of the constituents, or where there is excess of oxygen, there is a very appreciable chilling of the flame. In metal vessels 2·5 cm. in diameter, the percentage combustion for $2CO + O_2$ is about 90 per cent., in the presence of excess oxygen it is very slightly larger, but in the presence of excess of carbon monoxide (33 per cent.) the percentage combustion is practically 100 per cent. This is in accord with II., for carbon monoxide when present in excess will diminish the number of collisions of O_2^* with the walls and with deactivating molecules in the gas phase.

The Initiation of Flame by a Silica Surface.

A silica surface lowers the temperatures at which mixtures of carbon monoxide and oxygen will burst into flame. The extent of the lowering, however, depends very markedly on the state of the silica surface.[5] The other ignition phenomena are also affected by the condition of the surface. For example, Fig. 1 illustrates differences which can occur between two silica surfaces. In this figure, is given the percentage of the gaseous mixture, $2CO + O_2$, which undergoes instantaneous change into carbon dioxide on

[4] Cf. Mecke, Z. physik. Chem., 7B, 108, 1930; and Haber and Bonhoeffer, ibid., 263, 1928.
[5] Cosslett and Garner, Trans. Far. Soc., 26, 190, 1930.

introduction into a silica reaction chamber. The percentage combustion is plotted against the pressure of the gas admitted to the reaction vessel. Curve II. is that for an active, and Curve I. that for an inactive, surface. In the case of the inactive surface, the flame cannot be very extensive, since at pressures from 3 to 10 cm., the percentage combustion lies between 0 to 10 per cent. Under these circumstances, any flame is probably confined to a gas film near the walls. It will be observed that the ignition pressure differs for the two surfaces, which shows that the lower pressure limit is very largely a surface phenomenon.

The dependence of the ignition pressure on the state of the surface, indicates that there is some other factor entering into the phenomena of flame initiation, other than the temperature of the bulk of the gas and the starting of reaction chains from the surface. This, we believe, is the temperature of the surface layers.

A high ignition pressure is always associated with a low

FIG. 1.—Effect of surface on ignition.

rate for the stationary reaction. Under these conditions, little heat is generated near the surface, and consequently thermal activation in the surface layers is negligible, and the second term in equation 1a is small in magnitude. When there is a high rate of the stationary reaction, much higher temperatures are produced near the walls. This enables ignition to occur at low pressures.

Experimental.

The experimental technique adopted has been described previously.[5] An outline is, however, given below. A mixture of carbon monoxide and oxygen in the proportions 2 : 1 by volume was admitted into an evacuated silica tube maintained at constant temperature in the neighbourhood of 600° C. The admission was made as rapidly as possible through a wide bore tap connected by a ground joint to one end of the quartz tube, which was 20 cm. long and 3 cm. internal diameter. The internal area of the vessel was 200 sq. cm., and the volume of that part of the vessel which was at 610° C. was 142 c.c. The volume in the exit tubes and manometer was 25 c.c. The pressure of the gas was measured by means of a mercury manometer connected to the silica tube at its further end. Since the volume of the silica vessel and the leading tubes was known, any instantaneous combustion could be measured. By means of manometric read-

ings for 10 to 15 minutes, the stationary reaction in the neighbourhood of the surface could also be studied.

The activity of the silica surface was very variable, but could be brought back to a constant activity by keeping strictly to a routine of experimental procedure. The vessel was normally evacuated between two experiments for 30 minutes by means of Langmuir and Hyvac pumps through a wide bore tap. It was found in some experiments that prolonged exhaustion for 24 hours or more so modified the surface that on the admission of volumes of the combustible mixture to the exhausted surface, a decrease in volume occurred. This was shown subsequently to be mainly due to the adsorption of carbon monoxide. After 30 minutes exhaustion, the adsorption

Initial pressures, I., 12·7 cm.; II., 10·2 cm.; III., 7·67 cm.; IV., 5·12 cm.; V, 3·57 cm.
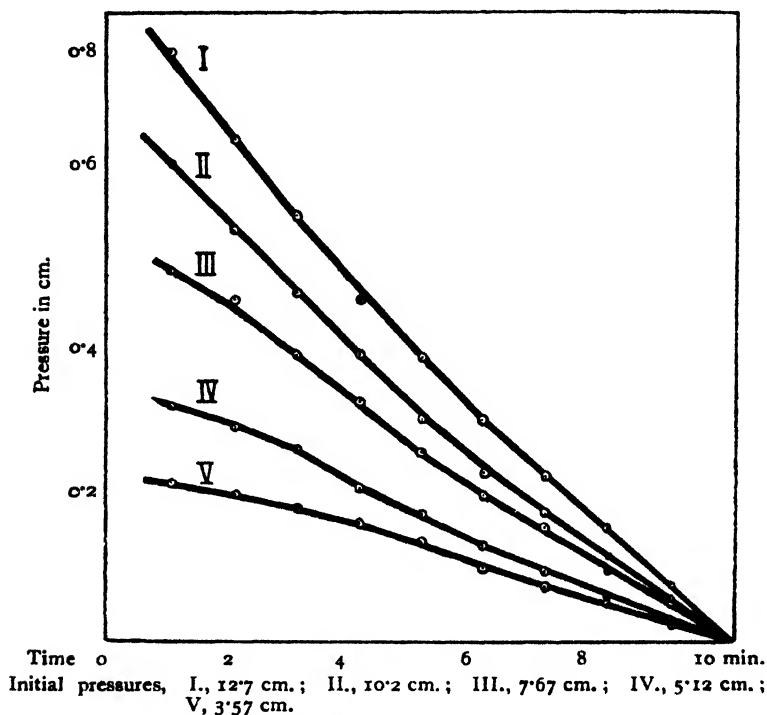
FIG. 2.—Nature of stationary reaction.

was found to be negligible, so that this interval was always allowed between successive experiments.

The gas was dried before admission by streaming over phosphoric oxide.

The Order of the Stationary Reaction.

The stationary reaction between carbon monoxide and oxygen was increased by packing the tube with silica wool.

The order of the reaction depended on the state of the silica surface. It varied between third and zero order. For an active surface it varied from the first to zero order, but when the surface was very inactive, the order of the reaction lay between three and two. The variation in the order of the reaction we believe to be due to the fact that the stationary

reaction is composite in character, occurring partly on the surface of the silica and partly in a gas film adjacent to the walls. With a silica surface as used in the following experiments, in which the surface was maintained at as constant activity as possible, the rate of decrease in pressure was nearly linear (Fig. 2, $3CO + O_2$).[6] In spite of the apparent zero order of the reaction, it was found, however, that the rate of the stationary reaction was proportional to the pressure. This indicates that the products are not without effect on the rate.

Information as to the nature of the stationary reaction has been obtained by the study of the effects of the addition of carbon monoxide, oxygen, nitrogen, argon and carbon dioxide to the equimolecular mixture.

Effect of Addition of Gases to the Equimolecular Mixture.

The phenomena studied are (a) the stationary reaction, (b) the lower critical ignition pressure, and (c) the rate of the stationary reaction at the ignition limit. Since the activity of the silica surface was likely to vary, it was necessary to bracket experiments with series on mixtures containing no diluent. The procedure adopted was as follows : First, a series of about ten experiments was carried out with the equimolecular mixture at pressures varying from 2 to 20 cm., and such series might be repeated several times until the surface had reached a steady state. This was followed by similar series with the diluted gas and finally by other series with the equimolecular mixture. Table I. shows a series of experiments carried out and the order in which they were done. The table gives the critical ignition pressure[7] and the rate of the stationary reaction at the ignition limit in arbitrary units.

For the surface in the standard state, the ignition pressure of $2CO + O_2$ is $7 - 9$ cm., and the maximum rate of the preflame reaction is $2 \cdot 0 \times 10^{-8}$ gm. mols. per sq. cm. per minute. 50 per cent. argon lowers the ignition pressure to $5 - 6$ cm. and lowers the preflame rate to $1 \cdot 5 \times 10^{-8}$ gm. mols. 50 per cent. O_2 lower the ignition pressure to $2 - 2 \cdot 5$ cm., but does not appreciably affect the preflame rate. CO raises the ignition pressure to $12 \cdot 5$ cm. and increases the preflame rate to $3 \cdot 1 \times 10^{-8}$ gm. mols. CO_2 has a curious effect (see Curve 8), but ignition occurs first at pressures similar to those in experiments with $2CO + O_2$. Nitrogen slightly raises the ignition pressure, and lowers the preflame rate to $1 \cdot 4 \times 10^{-8}$ gm. mols. per sq. cm. per minute. Curves showing the manner in which the rate of the stationary reaction varies with pressure are Figs. 3 to 7. The amount of fall in pressure in 10 minutes is plotted against the *total* pressure. The curves show an approximately linear rise from zero pressure up to the ignition limit. At the ignition limit there is an instantaneous decrease of volume on admitting the gases. This decrease is taken to be due to partial ignition, although in many cases no flame was visible to the eye. The percentage of ignition varies between $2 - 80$ per cent. of the total gas. It is never complete on account of the fact that a portion of the gas is outside the reaction vessel. Measurements of the stationary reaction were made after explosion had occurred. The ignition limit lies at the maximum on the above curves when the percentage of explosion is large, but this is not the case when the amount of ignition is small. In the latter case, the maximum rate for the stationary reaction occurs at pressures higher than the ignition pressure.

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[6] The change in pressure is shown over 10 minutes, the pressures after 10 minutes being arbitrarily taken as zero.
[7] Expressed as the total pressure of the gas.

TABLE I.—EFFECT OF FOREIGN GASES ON THE IGNITION PHENOMENA IN QUARTZ.

Gas Mixture.	Ignition Pressure. Cm.	Rate of Reaction at Explosion Limit. Cm. Hg. in 10 min. × 10⁴.
$2CO + O_2$	7·0	340
	9·5	340
	9·2	350
$2CO + O_2 + 20\cdot8$ per cent. Ar	7·8	220
	8·0	220
$2CO + O_2$	9·0	320
	9·0	340
$2CO + O_2 + 49\cdot8$ per cent. Ar	6·0	230
	5·8	265
	5·0	265
$2CO_2 + O_2$	7·0	330
	7·0	300
$2CO + O_2 + 50$ per cent. O_2 .	2·5	330
	2·5	330
Surface became less active.		
$2CO + O_2$	14·0	850
	12·0	580
	12·0	550
	9·5	400
$2CO + O_2 + 50$ per cent. CO .	12·5	850
	12·5	550
	12·5	520
$2CO + O_2$	9·5	350
	9·0	380
	7·5	350
$2CO + O_2 + 50$ per cent. O_2 .	2·5	—
	2·0	220
$2CO + O_2$	4·5	—
	5·5	—
$2CO + O_2 + 50$ per cent. CO_2	4·5 or 12·5	420
	4·5 or 12·5	380
$2CO + O_2$	5·5	380

Effect of Diluents on the Ignition Pressure, the Rate of the Preflame Reaction and the Percentage Combustion.

The addition of argon, oxygen, nitrogen, carbon monoxide to an equi-molecular mixture of carbon monoxide and oxygen produces very diverse effects on the phenomena of ignition, which it was not found possible to interpret without employing the theory embodied in equation V. The temperature in all cases was 610° C.

Argon.—Experiments were done in the following order: I., series with $2CO + O_2$; II., series with $2CO + O_2 + Ar$; and III., series with $2CO + O_2$. The addition of argon lowers the ignition pressure. The mean values for

the percentage combustion are recorded in Table II., the pressures of the *combustible* gas being given.

TABLE II.

Pressure in Cm. Hg. of Combustible Gas.	2·5.	3·6.	5·1.	7·7.	10·2.
I. $2CO + O_2$ per cent. .	—	0	10	35	58
II. $2CO + O_2 + Ar$.	0	14	32	50	63
III. $2CO + O_2$ . .	0	2	16	36	—

From this table, it is clear that argon increases the ignitability of the combustible mixture.

The rates for the stationary reaction are given in Fig. 3, expressed as pressure change in 10 minutes plotted against the *total* gas pressure. The rate of the stationary reaction is increased by the addition of argon if we consider partial pressures, but its main effect is seen in lowering the rate of
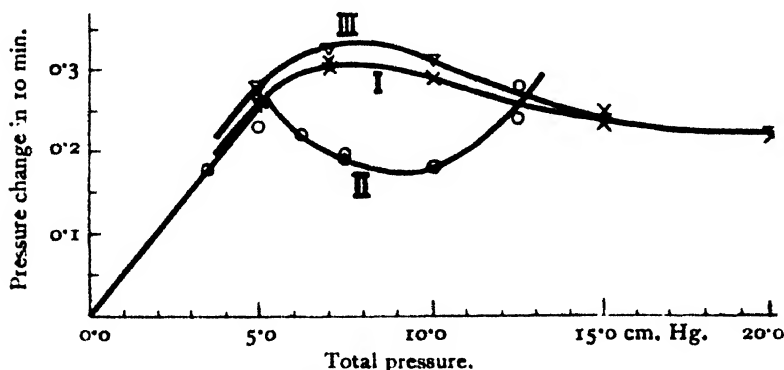
FIG. 3.—Effect of addition of argon.

the stationary reaction which is required before ignition occurs. Similar results were obtained with mixtures to which 20 per cent. argon had been added. The curves show a maximum at the ignition pressure. Up to this pressure, the rate of change is proportional to the pressure.

Since argon is not appreciably adsorbed on solid surfaces at 610° C., it is unlikely that there will be any effect produced by this gas, on the heterogeneous part of the stationary reaction (see equation V.). The increase in ease of ignition and the low rate of the stationary reaction at ignition must be due to the effect which argon has on the reaction in the gas layers adjoining the walls. There are two principal effects to be considered: (1) argon will lower the temperature of this film by virtue of its specific heat, and (2) it will compress the reaction chains within a shorter distance *d*. The reaction which does occur will therefore take place in a smaller volume than for the equimolecular mixture. Higher temperatures would be expected in the gas film as a result. The ignition temperature may thus be reached for smaller values of the rate of reaction when argon is present than when it is absent. On this account, ignition will occur at a lower pressure.

Nitrogen.—This gas would be expected to produce analogous results to those obtained with argon, that is, it should modify the phenomena in the gas film in a similar way to those given by this gas. The main

differences between the two gases would be expected to lie in their specific heats, since both are inert gases as far as the reaction is concerned; nitrogen has much the larger specific heat and hence will exert a more marked lowering on the temperature of the gas film by virtue of its specific heat than argon.

TABLE III.—PERCENTAGE COMBUSTION.

Pressure in Cm. Hg. of Combustible Gas.	2·5.	3·6.	5·1.	7·7.	10·2.
I. $2CO + O_2$ . . .	0	6	25	47	—
II. $2CO + O_2 + N_2$.	0	0	10	27	44
III. $2CO + O_2$ . . .	0	15	30	44	—

From Table III. it will be seen that on the addition of nitrogen, the ignitability of the gas is lowered and the ignition pressure raised.

In Fig. 4 are given the rates of the stationary reaction, I. and IV. being the curves for the equimolecular mixture [8] and II. and III. being curves for the mixture containing one volume of nitrogen. The rate of the stationary reaction is reduced by the diluent, but ignition occurs for a low value of the stationary reaction. The latter fact is important for the interpretation of the results. Stated in other words, it means that when nitrogen is present, the rate of reaction

FIG. 4.—Effect of addition of nitrogen.

necessary lfor ignition is· lower than that required for the ignition of the equimolecular mixture. This may be due to the compression of the reaction into a smaller volume by the nitrogen molecules, in which case, in order to account for the low rate of the stationary reaction, nitrogen

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[8] The surface was more active in these experiments than in the previous series.

must either diminish the rate of the heterogeneous reaction (term 1, equation V.) or break the reaction chains in the gaseous phase, *i.e.*, diminish n_1 the chain length.
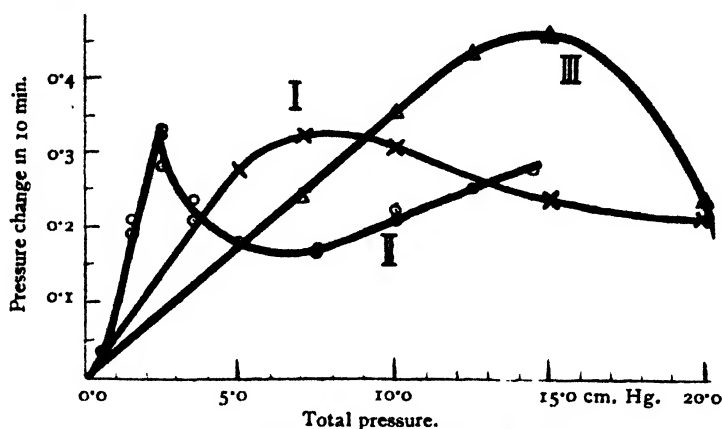
FIG. 5.—Effect of addition of excess oxygen.

Excess of Oxygen or Carbon Monoxide.

Since oxygen and carbon monoxide take part in the heterogeneous and homogeneous reactions, the effects due to the addition of these two
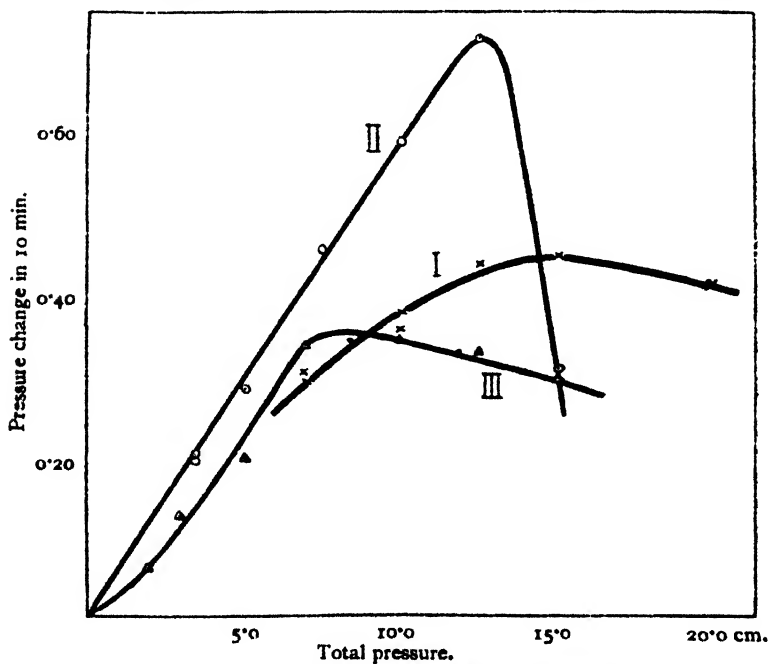
FIG. 6.—Effect of addition of excess carbon monoxide.

gases are likely to be complex. It is found that excess oxygen increases the ignitability of the gas and that excess carbon monoxide lowers it.

Oxygen.—Mixtures containing excess oxygen exert a marked effect on the silica surfaces so that experiments carried out after using the mixture, $2CO + 2O_2$, do not give the same results as when the surface is in the standard state.

TABLE IV.—Percentage Combustion.

Pressure in Cm. Hg. of Combustible Gas.	1·0.	2·0.	2·7.	3·6.	5·1.	7·7.	10·3.
I. $2CO + O_2$ per cent.	0	0	0	2	18	34	44
II. $2CO + O_2 + O_2$	0	0	39	54	65	66	66
III. $2CO + O_2$ per cent.	0	0	0	0	3	15	40

Excess oxygen lowers the pressure at which ignition occurs to below 2·5 cm., and it is evident from the above table that in the presence of excess oxygen the combustible gas is very easily ignited.

In Fig. 5 are given the rates of the stationary re-action plotted against the *total* pressure. Oxygen increases the rate of the stationary reaction, but does not affect the rate necessary for ignition. In this it differs from argon.
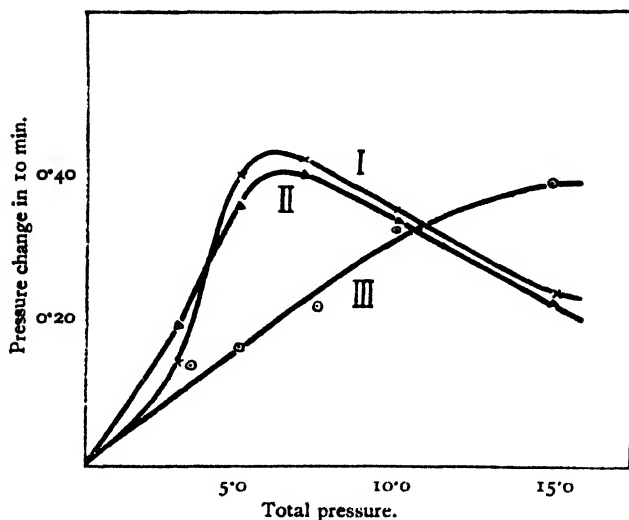
Fig. 7.—Effect of addition of carbon dioxide.

Carbon Monoxide.—Excess of carbon monoxide reduces the tendency for ignition. It raises the ignition pressure to above 10 cm. This is very surprising in view of the fact that it increases the rate of the stationary reaction (see Fig. 6). The reason for the difficulty of ignition is to be found in the fact that a very high rate of the stationary reaction must be reached before ignition is possible.

TABLE V.—Percentage Combustion.

Pressure in Cm. Hg. of Combustible Gas	2·5.	3·6.	5·1.	6·3.	7·7.	10·3.	13·5.
I. $2CO + O_2$	0	0	4	6	17	41	—
II. $2CO + O_2 + CO$	0	0	2	—	2	2	32
III. $2CO + O_2$	0	0	8	17	31	43	—

In the presence of carbon monoxide, the reaction must be spread out over a larger volume of gas than in the presence of excess oxygen. In other words, the chain length must be longer, which conclusion is in agreement with the mechanism set out on page   . Carbon monoxide must decrease the number of chains passing through unit volume of gas, otherwise ignition would occur at the normal rates for the stationary reaction. Thus it is difficult to avoid the conclusion that this gas retards the heterogeneous reaction and decreases the number of chains reaching the gas phase from the surface.

The differences between the behaviour of excess oxygen and excess carbon monoxide are readily interpreted if the chains are initiated by oxygen and the chain length is mainly increased by carbon monoxide. The increased rate of the stationary reaction in excess oxygen is then due to an increase in the number of reaction chains started from the surface, the increased rate in presence of excess carbon monoxide on the other hand being due to a lengthening of the chain.

Excess Carbon Dioxide.—If the conclusions made with regard to nitrogen are correct, the addition of carbon dioxide should reduce the rate of preflame reaction and increase the ignition pressure. This is correct except for a curious phenomenon shown in the results for the percentage combustion of the gases, Fig. 8. Curve I. is that for $2CO + 2O_2$; Curve II. that for $2CO + O_2$, and Curve III. that for
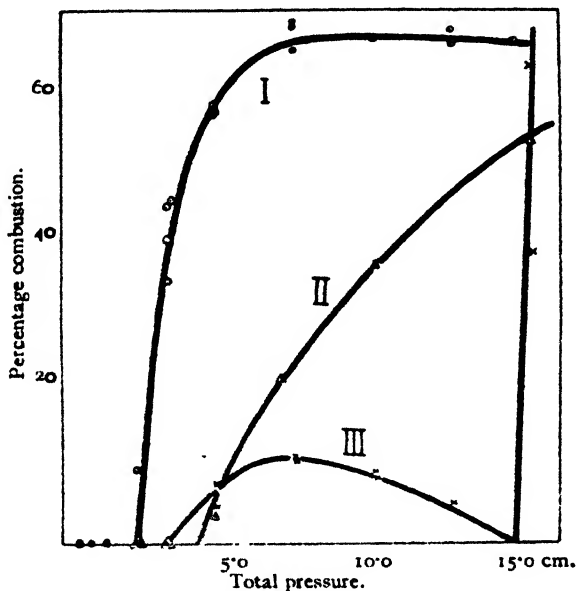
I. $2CO + 2O_2$.   II. $2CO + O_2$.   III. $2CO + O_2 + CO_2$.

Fig. 8.—Percentage combustion.

$$2CO + O_2 + CO_2.$$

It will be observed that the percentage combustion in Curve III. increases to a maximum and then decreases. We are able to offer no explanation of this.

Fig. 7 shows the rate curves for I. and II. $2CO + O_2$, and III. for $2CO + O_2 + CO_2$. CO_2 obviously decreases the rate of the stationary reaction.

Summary.

(1) The ignition phenomena which occur when dried carbon monoxide and oxygen mixtures are admitted to an evacuated silica vessel at 610° C. have been examined. The ignition pressures, rates of the stationary reaction, and the percentage combustion have been measured.

(2) The effects of the addition of O_2, N_2, CO, Ar, and CO_2 to the explosive mixture have been studied. O_2 and Ar increase the ignitability of the gaseous mixture, whereas N_2, CO and CO_2 reduce the ease of ignition.

(3) It is concluded that : —

(a) Both energy and reaction chains are present in flames.

(b) A flame to be stable must be backed by a sufficiently high temperature— the ignition temperature.

(c) The stationary reaction between carbon monoxide and oxygen on silica at 610° C. occurs partly on the surface and partly in the layers of gas adjoining the walls.   The rate of the reaction in the gas layers is dependent on their temperature.   An equation is given which expresses the rate of the stationary reaction, and in terms of this equation, an interpretation is given of the experimental results.

(4) A mechanism is given for the chain reaction in the gaseous phase which is in accord both with the ignition phenomena and with experiments on the chilling of flames in narrow cylindrical bombs.

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THE MOLECULAR CONSTITUTION OF THE η AND H SOLID ALLOYS AND OF THE CORRESPONDING LIQUID SOLUTIONS OF THE COPPER TIN SERIES EXAMINED THERMO-DYNAMICALLY.

By F. H. Jeffery.

The results from which the following calculations were made were obtained by the author using an electrical resistance method for which temperature and change of resistance were measured by two Callendar recorders.[1]

There was a well-marked "point saillant" on the liquidus at 13 atomic per cent. copper corresponding to the change of solid phase η to H; the isothermal line separating the η and liquid region from the H and liquid region has been taken to be at 411° C., the eutectic isothermal at 227° C. and the solidus separating the H and liquid region from the H and η region a curved line from 62 atomic per cent. copper at 411° C. to 41 atomic per cent. copper at 227° C.

Alloys corresponding to the η and liquid region were examined first. The work of previous investigators established that the solid η is the definite compound Cu_3Sn.   It seemed probable that the liquid phase might be a solution of the compound Cu_4Sn in tin, the tin consisting of monatomic molecules.   On this assumption η would be formed according to the equation

$$3Cu_4Sn + Sn = 4Cu_3Sn.$$

[1] *Trans. Faraday Soc.,* **23**, 566, 1927.

If n is the molal fraction of Cu_4Sn in the liquid solution

$$\nu_0 \log (1 - n) + \nu_1 \log n = \log K,$$

where

$$\nu_0 = -1, \quad \nu_1 = -3.$$

Hence

$$- \log (1 - n) - 3 \log n = \log K,$$

also

$$\frac{\partial}{\partial \theta} \log K = \frac{-\lambda}{R\theta^2}.$$

The integration is

$$- \log (1 - n) - 3 \log n = \frac{\lambda}{R\theta} + \left(\log K_{\theta_1} - \frac{\lambda}{R\theta_1} \right),$$

where θ_1° is close to 684°, it being supposed that the solutions are sufficiently dilute, and that λ is sensibly constant and has the value for θ_1. Hence if the molecular constitutions of the liquid and solid phases have been correctly chosen $- \log (1 - n) - 3 \log n$ is a linear function of $\frac{1}{\theta}$.

The results shown in Table I were obtained :—

TABLE I.

θ.	Atomic Per Cent. Copper in Liquid.	n.	$\log (1 - n) + 3 \log n$.	$\frac{1}{\theta}$.
691	14	$4 \cdot 07 \times 10^{-2}$	$\bar{5} \cdot 811$	$1 \cdot 447 \times 10^{-3}$
706	16	$4 \cdot 76$	$\bar{4} \cdot 012$	$1 \cdot 416$
718	18	$5 \cdot 49$	$\bar{4} \cdot 194$	$1 \cdot 393$
730	20	$6 \cdot 25$	$\bar{4} \cdot 370$	$1 \cdot 370$
743	22	$7 \cdot 05$	$\bar{4} \cdot 513$	$1 \cdot 346$
755	24	$7 \cdot 90$	$\bar{4} \cdot 656$	$1 \cdot 324$
767	26	$8 \cdot 78$	$\bar{4} \cdot 791$	$1 \cdot 304$

These points lie sensibly on the straight line through the first and fifth.

This affords evidence that the liquid phase consists of Cu_4Sn dissolved in monatomic tin molecules, the solid phase being the pure compound Cu_3Sn.

The solid phase H did not appear to be a definite chemical individual inasmuch as the solidus from the eutectic isothermal to the 411° C. isothermal as determined by the author is a curved line suggestive of a solid solution. It seemed that this H might be a solid solution of Cu_3Sn in tin, the tin consisting of monatomic molecules. The liquid phase was again assumed to be a solution of Cu_4Sn in monatomic tin molecules, there being no evidence of any discontinuity in the liquid phase as the temperature changed through 411° C. With these assumptions the solid phase would be formed from the liquid phase according to the reaction

$$3Cu_4Sn + Sn = 4Cu_3Sn.$$

If n is the molal fraction of Cu_4Sn in the liquid phase and n' the molal fraction of Cu_3Sn in the solid phase

$$\nu_0 \log (1 - n) + \nu_1 \log n + \nu_0' \log (1 - n') + \nu_1' \log n' = \log K$$

where

$$\nu_0 = -1, \quad \nu_1 = -3, \quad \nu_0' = 0, \quad \nu_1' = 4.$$

Hence $- \log (1 - n) - 3 \log n + 4 \log n' = \log K$

$$= \frac{\lambda}{R\theta} + \left(\log K_{\theta_2} - \frac{\lambda}{R\theta_2} \right),$$

where $\theta_2°$ is close to $500°$, the reasons for this mode of integration being similar to those given previously.

The results shown in Table II. were obtained :—

TABLE II.

θ.	Atomic Per Cent. Copper in Liquid.	Atomic Per Cent. Copper in Solid.	n.	n'.	$- \log (1 - n)$ $- 3 \log n + 4 \log n$.	$\frac{1}{\theta}$
507	1·5	45·0	$3·81 \times 10^{-3}$	$2·73 \times 10^{-1}$	5·003	$1·972 \times 10^{-3}$
517	2·0	48·5	5·10	3·14	4·867	1·934
526	2·5	50·3	6·41	3·37	4·695	1·901
535	3·0	51·7	7·73	3·57	4·548	1·869
544	3·5	52·6	9·07	3·70	4·404	1·838
552	4·0	53·4	10·42	3·82	4·279	1·812
561	4·5	54·4	11·78	3·98	4·189	1·782
570	5·0	55·0	13·16	4·07	4·088	1·754
586	6·0	56·4	15·96	4·31	3·937	1·706

The first six points lie sensibly on the straight line through the third and sixth ; the next three points slowly diverge from this straight line, but in a manner such as might be expected for solutions of increasing concentrations beyond the applicability of the thermo-dynamic equation. The high concentrations of the solid solutions for which the equation appears to be applicable are noteworthy.

This affords evidence that the liquid phase is a solution of Cu_4Sn in tin, the latter existing as monatomic molecules and that the solid phase is a solid solution of Cu_3Sn dissolved in monatomic molecules of tin.

Discussion of these Results.

In a previous paper[2] the author gave evidence showing that the liquid alloys of concentrations up to 15 atomic per cent. tin at temperatures down to 800° C. were solutions of the compound Cu_4Sn, this coupled with the results just described makes it probable that all liquid alloys of compositions given by the portion of the diagram on the copper side of the eutectic are solutions of this compound.

The solid H appears to be a solid solution of the compound Cu_3Sn in tin and not a definite chemical individual, it will be noticed that for the concentrations of the solid solutions examined the mean composition roughly approximates to the value one gram atom of copper to one gram atom of tin.

The consistence of the results given by the thermo-dynamic equations affords evidence that the phase boundaries from which they were calculated have been determined with substantial accuracy by the electrical resistance method used, grave errors would make it impossible to find any thermo-dynamic equations to satisfy the boundary conditions.

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[2] *Trans. Faraday Soc.*, **27**, 136, 1931.

REVIEWS OF BOOKS.

An Account of the Principles of Measurement and Calculation. By
N. R. CAMPBELL. (London : Longmans, Green & Co., 1928. Pp. ix+293.
Price 12s. 6d.)

Dr. Norman Campbell is the Fat Boy of modern physics—he wants to make
our flesh creep, and really he does so on occasion with no uncertain measure of
success. His volume on " Measurement and Calculation " is a thoroughly
stimulating and unorthodox work, and Dr. Campbell is never more stimulating
than when, in the eyes of the serious-minded and conventional, he is most wrong-
headed. We know how the ordinary volume meanders through this series of
topics—we have all done it, or thought about it. How to take a reading ;
averages, with a " fudge " concerning the arithmetic mean and the most probable
value ; probable errors and standard deviations ; the Gaussian Law and the
cocked-hat curve ; unsymmetrical distributions ; weights ; . . . κτλ. And in
practical politics, much notice we take of the whole melancholy business !

Dr. Campbell's book is concerned with this type of matter, and with a good
deal more. He would make philosophers of us, willy-nilly, and he leads off with
two chapters on the fundamental laws of measurement. We are not inclined
to take Dr. Campbell *au grand serieux* in his introductory discussion ; his
definitions require a good deal of illustration to help them out (in some instances
we find logical terms used in a sense which is not quite that in which the formal
logician uses them), and we are left with a feeling that he would not have us
waste time in criticising the portico, but enter the temple forthwith. Spencer, if
we remember rightly, exhibited the same amiable anxiety.

But when, leaving this introductory matter, Dr. Campbell comes to deal with
Numerical Laws, Derived Measurements, Errors of Measurement, Errors of
Numerical Laws, Calculation and the like, he has much to say that may well be
pondered and studied critically, even if we shy at such extreme statements as " I
reject then the Gaussian Theory of Error, without qualification, and with the
utmost possible emphasis."

In particular, we would commend his chapter on the Theory of Dimensions
to those who are accustomed to use that theory without sufficient discrimination.

But equally it will not answer to pay overmuch attention to these problems
of measurement. Most of us do, somehow or other, manage to take fairly
reliable measurements and to calculate out results. And while we are grateful
to Dr. Campbell for pointing out these pitfalls for straying feet, it is well also to
be mindful of the fate of the centipede, who

> " was happy quite
> Until the frog, for fun,
> Asked her which leg went after which,
> Which raised her doubts to such a pitch,
> She died distracted in a ditch,
> Not knowing how to run."

A. F.

The Quantum and Its Interpretation. By H. S. ALLEN. (London :
Methuen & Co. Pp. xii + 214. Price 12s. 6d.)

Despite the kaleidoscopic manner in which our views on modern physics
form, change and dissolve, there is a foundation sufficiently permanent to make
it worth while to present views of the Quantum to students who are not in the
van of modern knowledge, and whose mathematical equipment, while a little more
than elementary, is still far from profound. Professor Allen is a born teacher
and wise in all those difficulties that confront an inquiring student. His book is

confessedly not a treatise on quantum theory, but an attempt at a resolution of a problem possibly—nay, probably—inherently insoluble—that of the nature of the quantum.

Nevertheless it is expounded with such art, with such a wealth of historical knowledge, and with, on the whole, such balanced judgment (though a surly critic might cavil at the space given to Edinburgh) that the book will be welcomed as a reliable guide to the elements of the quantum theory by many a worried student. And despite the chops and changes of modern theory its basis is sufficiently sure to make it, with due alterations and additions, a text-book for a number of generations of students to come.

It is impossible, within the limits of a brief review to do more than barely sketch the scope of the book, which is divided into three sections. Part I. deals with fundamental principles and includes a preliminary survey of the main features of the problem, an account of atomicity in electricity and magnetism, of line spectra, and of atomic structure.

Part II. deals with special investigations, and Part III., which discusses the development of the quantum theory, includes chapters on Planck's constant, the structure of radiation, the Zeeman effect, the spinning electron and wave mechanics.

In the matter dealt with in these latter chapters the chosen theory of to-day is often but a battered ruin tomorrow, and it is here that changes will most frequently be necessary.

The book can be heartily recommended, and it is hoped that future editions, in which these changes may be duly recorded, will follow in due course.

A. F.

Gunterschulze. Electric Rectifiers and Valves. Translated and revised by N. A. DE BRUYNE. (London : Chapman & Hall, 1927. Pp. xiii + 212. Price 15s.)

A treatise on valves and rectifiers can usefully fill a corner of the library of the research physicist or " Techniker." As the author points out, broadcasting has brought about a demand for small rectifiers, while the growth of large A.C. stations has emphasised the importance of mercury arc rectifiers.

The author, realising the necessity for a firm grasp of physical principles in handling valve theory, divides the book into two parts. The first part elaborates the physical basis of valve action and includes chapters on classification, atomic structure (a little hazy here and there), conduction in gases, actions at the anode and cathode, and the arc discharge.

The technical section opens with a chapter on the mathematical theory of valves, and goes on to deal in detail with mechanical, electrolytic, glow discharge and mercury vapour rectifiers, concluding with chapters on the properties of rectifier installations, on miscellaneous types and on various applications of valves.

The translation is competently done, and the translator has slightly extended the scope of the book. Here and there the translation has a distinctly teutonic flavour. The sentence (p. 52), " The electrons production of the cathode spot of an arc is the most productive method of all," we leave without comment. " No marked dissociation can exist in a gas *per se*," is a remarkable effort, and teutonisms such as " a much greater voltage is necessary to send a given current strength through the gas as when free electrons are available " should be eliminated in a second edition.

A. F.

THE PROPERTIES OF SEWAGE COLLOIDS.

By E. C. C. BALY, C.B.E., F.R.S.

The literature dealing with sewage and sewage disposal contains little information as to the properties of the substances present in colloidal solution. It would seem that a knowledge of these properties is of considerable importance in relation to the activated sludge process of sewage disposal and the activated filter bed method of water purification. Especially is this true as regards the sign of the electric charge owing to the undoubted presence of protein substances in sewage.

One of the most attractive theories of the activated sludge process is that the purification is caused by the mutual coagulation of colloids of opposite charge, but this theory appeared to be definitely negatived by the observations of Buswell and Long. These authors [1] found that both sewage colloids and activated sludge particles were, so far as they were able to determine, electronegatively charged. In view of the fact that some at any rate of the colloids must be proteins and therefore have an iso-electric point it appeared advisable to determine the sign of the electric charge with various hydrogen ion concentrations.

In this investigation two methods have been employed. In the first place the flocculation of suspensions of various inorganic powders carrying an electric charge of known sign was observed, and in the second place the sign of the electric charge on the sewage colloids was directly determined by means of cataphoresis measurements.

The validity and accuracy of the flocculation method was first tested by means of two colloids of known iso-electric point, namely pure gelatin and hæmoglobin, the iso-electric points of which are at $p_H = 4\cdot8$ and $6\cdot8$, respectively. Suspensions of a fine silt and of bentonite were employed, both of which had been proved by cataphoresis observations to be electronegatively charged, and these were adjusted to various values of p_H. In the case of iso-electric gelatin the suspensates were rapidly flocculated by the gelatin when the p_H was $4\cdot6$ and less, no measurable effect being observed when the p_H was greater than $4\cdot8$. The suspensions were rapidly flocculated by hæmoglobin when the p_H was less than $6\cdot8$, no effect being noted when the p_H was greater than $6\cdot8$. I am indebted to Dr. B. N. Ghosh for having carried out these observations.

The determinations with sewage colloids were made in exactly the same way. The sewage used was collected at about 9 a.m. whenever required and was filtered through coarse filter paper before use. The observations were always carried out shortly after the sewage had been collected for reasons which will presently be understood. Suspensions of fine silt and of

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[1] *Proc. Amer. Waterworks Assoc.,* 309, 1923.

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bentonite were used and adjusted to various p_H values, and after the addition of the sewage the final p_H was determined electrometrically.   In the first series of observations the final dilution of the sewage was $1 : 15$ and the concentration of the suspensate was $0·33$ per cent.   Under these conditions it was found that the colloids in sewage have an iso-electric point at about $p_H = 4·6$, since it was found that the addition of sewage had no effect when the p_H was greater than $4·6$, and caused a rapid flocculation and sedimentation of the suspensate when the p_H was less than $4·6$.

The observations were several times repeated with greater dilutions of the sewage with identical results, and it is remarkable how delicate is the flocculation test.   The addition of 1 c.c. of sewage to 300 c.c. of a suspension containing $0·003$ grm. of bentonite causes visible flocculation within one minute when $p_H = 4·4$.   When the volume of sewage is 3 c.c. the flocculation is visible within a few seconds.

An interesting fact was noted in that the iso-electric point of sewage colloids is apparently shifted towards larger p_H values in presence of 3 per cent. sodium chloride.   Owing to the flocculating action of electrolytes on the suspensions used it was of course necessary to have controls with which to compare the suspensions containing sewage.   For each of the values of p_H two cylinders were used containing 300 c.c. of the suspension in 3 per cent. sodium chloride and to one of these 20 c.c. of sewage were added. A range of p_H values between 10 and $3·5$ was adopted, and it was found that when the p_H was greater than $8·3$ the addition of sewage produced no effect, and that rapid flocculation and sedimentation was caused by the sewage when the p_H was less than $8·3$.   It may be stated that the flocculating effect of sewage was far greater than that of the electrolyte, and that in no case was there any doubt as to the effect or absence of effect of the sewage.   These results indicate that in the presence of 3 per cent. sodium chloride the iso-electric point of sewage colloids is apparently shifted to $8·3$. These observations were confirmed with many electronegative suspensions other than those of fine silt and bentonite.

Dr. B. N. Ghosh was kind enough to determine whether a similar shift in the iso-electric point took place with saline solutions of iso-electric gelatine.   He found that the addition of gelatin[2] markedly increased the flocculation of a suspension of bentonite in 3 per cent. sodium chloride solution when the p_H was as great as 6.   It would seem, therefore, that the effect of electrolytes is not peculiar to sewage colloids.

The foregoing results have been confirmed by cataphoresis measurements. In each observation the conductivity of the sewage was determined and the aqueous layers above the sewage were adjusted to the same conductivity by the addition of sodium chloride, and silver-silver chloride-sodium chloride solution electrodes were used.   In order to guard against any possible complication due to the electronegatively charged bacteria present, the sewage was sterilised by the addition of $0·2$ per cent. formaldehyde.

In the case of fresh sewage, which had a conductivity equivalent to that of $0·15$ per cent. sodium chloride solution, it was found that the colloids migrated towards the anode when the p_H was 7 or greater than 7.   When the p_H was 6 and less than 6 the colloids migrated towards the cathode. An accurate determination of the iso-electric point was not possible since with values of p_H between 6 and 7 the boundary surfaces tended to become indistinct.   There is, however, little doubt that the iso-electric point was not far from $p_H = 6·5$.

[2] *Trans. Chem. Soc.*, 2285, 1929.

After the addition of 3 per cent. sodium chloride to the sewage it was found that no movement of the colloids took place at $p_H = 8\cdot3$, and that the colloids moved towards the cathode at $p_H = 7\cdot7$ and towards the anode at $p_H = 9$.

The foregoing results obtained by two independent methods may be summed up as follows: when filtered sewage is diluted with 15 times its volume of distilled water, the colloids have an iso-electric point at $p_H = 4\cdot6$, which is not far different from that of gelatin. In the presence of $0\cdot15$ per cent. sodium chloride the iso-electric point lies at about $p_H = 6\cdot5$, and at $p_H = 8\cdot3$ in the presence of 3 per cent. sodium chloride. It may be pointed out that since fresh sewage has $p_H = 7\cdot4$ and since the iso-electric point is at $p_H = 6\cdot5$, the colloids in sewage are electronegative. This agrees with the observation recorded by Buswell and Long.[1]

The results now recorded are of particular interest when the bacteria present in sewage are considered. It is known that these organisms are electronegatively charged, and it follows that when the p_H is smaller than that corresponding to the iso-electric point the bacteria and electropositive colloids must have some mutual influence. The most probable result of this mutual influence will be that when the concentration of the bacteria is relatively small, as is the case in fresh sewage, there will exist in solution bacteria-colloid com-plexes. Since the p_H of fresh sewage is smaller than the iso-electric point ($p_H = 8\cdot3$), evidence should be obtained of the existence of two types of particles in unsterilised sewage to which 3 per cent. sodium chloride has been added, namely, electropositive col-
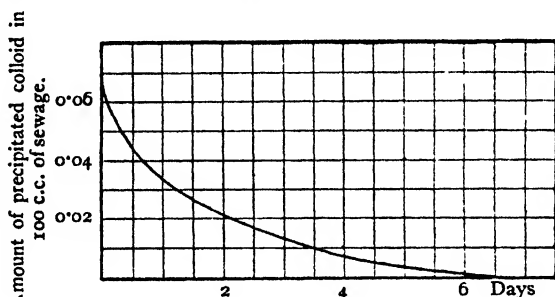
FIG. 1.

loids and bacteria-colloid complexes carrying a smaller electropositive charge. Furthermore, if the saline sewage be kept under aerobic conditions in order to permit bacterial reproduction a stage should be reached when the bacteria are flocculated by the colloids to produce a bacterially active sludge. Experimental observations show that these conditions actually obtain.

In the first place it was found that the flocculating power of sewage on fine suspensions rapidly decreases with the age of the sewage. If the fresh sewage is kept under aerobic conditions the multiplication of the bacteria causes a rapid decrease in the amount of free colloid present with the result that on the seventh day the sewage no longer causes any flocculation of suspensions in 3 per cent. sodium chloride solution with $p_H = 7$. The rate of decrease in the amount of colloid that can be precipitated in this way is shown in Fig. 1.

In the second place, the flocculation of the bacteria by the colloids can readily be observed in the following way which was suggested to me by Dr. Adeney. To 9 litres of 3 per cent. sodium chloride are added 300 c.c. of fresh sewage which has been filtered through coarse filter paper and the whole is vigorously stirred in a large open dish, this being the most satis-factory method of securing the saturation of the solution with oxygen. The solution remains clear for about 90 hours and then there begin to

separate flocks which are very bacterially active.   These flocks increase in volume until the fifth day when no further change appears to take place. The bearing of this self-flocculation of sewage liquor on the activated sludge process is discussed in a separate communication.[3]

When a suspension of a fine inorganic powder is flocculated by sewage at a p_H smaller than that corresponding to the iso-electric point, the flocculated precipitate contains sewage colloids, and a quantitative study of this has led to results which are of some interest in the present connection. Although the co-precipitate of suspensate and colloid is doubtless due to adsorption, the process is irreversible since it is not possible to remove the colloid from the precipitate by washing with water.   Indeed the co-precipitate is remarkably stable.   As was to be expected it was found that with a given volume of sewage liquor the amount of colloid in the co-precipitate
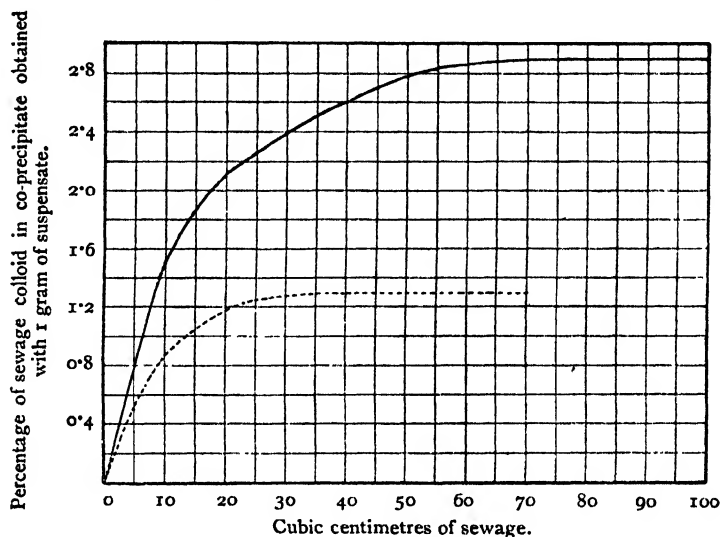
Fig. 2.

formed with a constant weight of suspensate varied with the fineness of grade of the suspensate and in consequence it was found necessary to use a small quantity of suspensate and to determine the amount of colloid in the whole of the co-precipitate formed on the addition of different amounts of sewage liquor.   Two suspensates were used, namely a fine silt and pure manganese carbonate.   A typical series of determinations may be described. Four lots of 1 gram of silt were suspended in 20 c.c. of water and to each of these suspensions were added, respectively, 10 c.c., 20 c.c., 35 c.c., and 60 c.c. of sewage liquor, each of these volumes having been diluted to 200 c.c. with 3 per cent. sodium chloride solution.   The precipitate was in each case washed and dried at 100° C., and the amount of colloid present was determined by the loss in weight on ignition, the loss in weight suffered by the silt on ignition having previously been determined.   The results are given in Table I.

[3] *J. Soc. Chem. Ind.*, 50, 22, 1931.

TABLE I.

Volume of Sewage. (c.c.)	Total Loss on Ignition.	Loss on Ignition of the Silt.	Amount of Sewage Colloid.
10	4·54	3·10	1·49
20	5·15	3·10	2·12
35	5·53	3·10	2·51
60	5·88	3·10	2·87

The relation between the amount of colloid in the precipitate and the volume of sewage liquor is expressed by the full curve in Fig. 2, the dotted curve showing the relation when suspensions were used of manganese carbonate, the particles of which are larger than those of the silt.

Since it may be assumed that 1 gram of silt is capable of removing the whole of the colloid present in 1 c.c. of sewage liquor (an assumption subsequently found to be justified), it is possible from the full curve in Fig. 2 to calculate the fraction of the total colloid present in 100 c.c. of sewage precipitated by different amounts of the silt. The calculated quantities are given in Table II. and the relation between the amount of silt and the fraction precipitated of the total colloid present is shown by the curve in Fig. 3.

TABLE II.

Weight of Silt (Grams).	Percentage Amount Precipitated of Total Colloid Present.	Weight of Silt (Grams).	Percentage Amount Precipitated of Total Colloid Present.
0·20	5·00	7·00	77·75
0·50	12·00	8·00	83·40
0·75	15·50	9·00	87·50
1·00	19·75	10·00	90·30
1·50	26·23	15·00	94·00
2·00	33·70	20·00	94·55
2·50	39·50	25·00	95·25
3·00	44·91	50·00	98·50
4·00	55·15	60·00	98·95
5·00	64·24	100·00	100·00
6·00	71·00		

These values, with the exception of the last three, are expressed by the curve in Fig. 3.

This curve shows the remarkable rapidity with which the amount of colloid precipitated falls after about four-fifths has been removed, the last fifth requiring a very great increase in the amount of suspensate for its complete precipitation. In short, the results indicate the presence of two types of colloid in fresh saline sewage, the two types differing greatly in the readiness with which they are precipitated with a fine suspensate.

As was pointed out above this is exactly the result to be expected with fresh saline sewage in which the concentration of the bacteria is small enough to be outside the flocculation zone.

Further evidence of the existence of the two types of colloid in fresh saline sewage has been obtained. These two types consist of free colloid carrying a relatively large electropositive charge, and of bacteria-colloid

complexes carrying a relatively small electropositive charge. The former should be selectively precipitated when a given volume of fresh saline sewage is added to a small quantity of silt in suspension whereas the latter should only be brought down when the same volume of sewage is added to a large quantity of silt in suspension. The co-precipitate in the one case should be free from bacteria and in the other case bacterially active. For convenience in handling the co-precipitate, two lots of 50 grams of silt in aqueous suspension were added to 100 c.c. and 1000 c.c. respectively, of fresh sewage containing 3 per cent. of sodium chloride.

The results are set forth in Table IV.

TABLE IV.

Weight of Silt. (Grams.)	Volume of Sewage. (c.c.)	Amount of Colloid in Co-precipitate. (Per Cent.)	Fraction of Total Colloid Precipitated. (Per Cent.)	Properties of Co-precipitate.
50	1000	2·12	64·2	Bacterially inactive
50	100	0·20	98·5	Bacterially very active

The two co-precipitates were collected on Buchner funnels and tested in two ways for the presence of bacteria. In one case both were treated on the filter with a solution of Witte's peptone, when the second precipitate rapidly gained in its content of organic matter up to 3·5 per cent., the first precipitate remaining unchanged. In the other case the two precipitates were kept moist under fully aerobic conditions. Once again the first precipitate underwent no change, whilst the second underwent marked changes in physical properties, these changes being accompanied by a small increase in the organic matter present. These results clearly indicate that the co-precipitates prepared by flocculating an inorganic suspensate with an excess of fresh saline sewage are bacterially inactive and that co-precipitates prepared by treatment of fresh saline sewage with an excess of the suspensate are bacterially active.

A final proof is given by the fact that when an organic suspensate is flocculated by an excess of fresh saline sewage the filtrate still contains the bacteria, and that when fresh saline sewage is treated with a large excess of the suspensate the filtrate is completely sterile.

Weight of silt in grams.

72
64
56
48
40
32
24
16
8

0   20   40   60   80   100

Percentage amount co-precipitated of total sewage colloid.

FIG. 3.

During the early course of these observations a very remarkable fact was observed when Hartwell clay was used as a suspensate. This clay gave on ignition a loss in weight of 4·48 per cent. and suspensions of it were flocculated by fresh saline sewage in small quantities. The bacterially active co-precipitate was collected on a Buchner funnel and kept moist when a small increase in the organic matter took place. The precipitate which had then become very compact and strongly coherent was allowed to remain, the conditions in the interior of the mass being anærobic. A sample taken from the interior of the mass on the fourth day showed a loss in weight on ignition which was considerably smaller than that given by the Hartwell clay itself. The analytical results are set forth in Table V.

TABLE V.

	Loss on Ignition of Co-precipitate Per Cent.	Loss on Ignition of Hartwell Clay Per Cent.	Amount of Sewage Colloid Present Per Cent.
Freshly prepared	6·68	4·48	2·30
After 24 hours	6·77	4·48	2·40
After 72 hours	6·90	4·48	2·53
After 96 hours	3·52	4·48	? *

* The last sample was taken from the interior of the mass.

The last result is a remarkable one and led to the view that the clay itself contained some organic matter which was utilised by the bacteria as food. This was found to be the case since the Kjeldahl method indicated the presence of 0·05 per cent. of nitrogen, the ratio of nitrogen to the loss in weight on ignition being 1·12 per cent. This ratio is a definite indication of the presence of organic matter. Further investigation showed that several natural clays contain nitrogenous organic matter, and it may be suggested that these clays were formed by a process of flocculation by organic colloids derived possibly from peat or, in the case of estuarine or marine clays from animal sources.

Typical clays containing organic matter are the salt marsh clays and in one of them, namely a clay from Sedney Drove End, the loss of weight on ignition was 9·29 per cent. and the amount of nitrogen (Kjeldahl) was 0·16 per cent. The ratio of nitrogen to the loss in weight on ignition is 1·72 per cent. The ratio of nitrogen to "volatile" matter has been used by analysts as an indication of the contamination by sewage of deposits in estuaries and tidal rivers. The high values given by the two above mentioned clays show that little reliance can be placed upon this ratio as a proof of sewage contamination.

It has been found possible to differentiate between the various types of organic matter by an application of the Adeney and Dawson process of oxidation by chromic acid.[4] Not more than 0·5 gram of the very finely powdered clay or deposit is added to a mixture of 50 c.c. $N/4$ potassium bichromate, 25 c.c. concentrated sulphuric acid and 25 c.c. water. The mixture is heated and kept in gentle ebullition for 2 hours, a little distilled water being added from time to time as the solution becomes too concentrated. After cooling, the solution is titrated with $N/4$ ferrous ammonium sulphate and the amount of oxygen consumed by the clay is determined.

[4] *Proc. Roy. Soc.*, Dublin, **18**, 199, 1926.

The ratio of this amount of oxygen to the nitrogen content (Kjeldahl) of the clay gives an indication of the nature of the organic matter present. Some results are given in Table VI., the values being given for 100 grams of each substance.

TALE VI.

Substance.	Oxygen. (Grams.)	Nitrogen. (Grams.)	Oxygen/Nitrogen Ratio.
Gelatin	132·4	18·0	7·3
Sedimented sewage liquor .	28·0	4·0	7·0
Sewage-silt co-precipitate .	6·78	0·45	15·3
Fenland clay . . .	3·60	0·16	22·5
Creechbarrow clay . .	3·68	0·08	46·0

The values for gelatin and sedimented sewage liquor are taken from Dr. Adeney and Miss Dawson's paper, and it must be remembered that in the case of the sewage liquor the organic matter in true solution as well as that in colloidal solution is concerned. The Fenland clay has probably resulted from flocculation by colloids of marine, *i.e.*, lower animal, origin. It certainly has not been derived from peat colloids because it contains no humus. The Creechbarrow clay, on the other hand, contains humus which may be extracted with warm sodium hydroxide solution. The organic matter contained in this clay must, therefore, have been of vegetable origin. The divergence between the O/N ratios for organic colloids of higher animal, lower animal, and vegetable origin is very marked and affords a means of differentiating between the three types.

Conclusions.

1. The sign of the electric charge on sewage colloids has been determined by the flocculation and cataphoresis methods.

2. In presence of very small quantities of electrolytes sewage colloids possess an iso-electric point of about $p_H = 4·6$. In the presence of 0·15 per cent. NaCl the iso-electric point lies at about $p_H = 6·5$, and at $p_H = 8·3$ in the presence of 3 per cent. NaCl.

3. A similar shift in the iso-electric point of gelatin in the presence of 3 per cent. NaCl has independently been observed.

4. In unsterilised saline sewage when the colloids are electropositively charged, the conditions are complicated by the presence of the electronegatively charged bacteria.

5. Quantitative determinations of the flocculation of fine suspensates by different amounts of fresh saline sewage indicate the presence of two types of colloid particles, one having a larger electropositive charge than the other.

6. These two types consist of free colloid particles and bacteria-colloid complexes.

7. Co-precipitates prepared by the flocculation of fine suspensates by excess of fresh saline sewage are bacterially inactive, whereas those obtained by the flocculation of an excess of fine suspensates by the saline sewage are very bacterially active.

8. When fresh sewage is kept, the amount of precipitable colloid therein rapidly decreases and becomes vanishingly small in about 7 days.

9. When fresh sewage diluted with 30 volumes of 3 per cent. NaCl solution is kept under the optimum aerobic conditions, the bacterial concentration increases until after 4 days they are flocculated by the electropositive colloids.

10. The analytical results obtained with co-precipitates of sewage colloid with certain natural clays indicated presence of organic matter in the clays.

11. It is suggested that these clays are the result of the flocculation of fine mineral suspensates by colloids of marine, animal or vegetable origin.

12. A method is described for the differentiation of colloids of higher animal, lower animal, and vegetable origin present in materials flocculated by these colloids.

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A VISCOSITY PARADOX.

By Professor E. N. da C. Andrade.

Received 13th March, 1931.

For some experiments on the effect of an electric field on the viscosity of liquids, it was necessary to calculate the axial flow of a viscous liquid in the space between two concentric cylinders. If the radii of inner and outer cylinders are r_0 and r_1 the formulæ [1] come out to be

$$u = \frac{P}{4\eta l}\left[-r^2 + \frac{r_1^2 - r_0^2}{\log r_1/r_0}\log r - \frac{r_1^2 \log r_0 - r_0^2 \log r_1}{\log r_1/r_0}\right] . \quad (1)$$

$$V = \frac{\pi P}{8\eta l}(r_1^2 - r_0^2)\left[r_1^2 + r_0^2 - \frac{r_1^2 - r_0^2}{\log r_1/r_0}\right] . \qquad . \qquad . \qquad (2)$$

where u is the velocity at any point distant r from the axis of the tube, V is the volume discharged per second, η is the coefficient of viscosity, P the difference of pressure at the two ends of a tube of length l. If in (2) we make r_0 zero, we get

$$V = \frac{\pi P}{8\eta l}r_1^4,$$

which is the ordinary formula for the discharge from a tube of radius r_1.

While at first sight it seems natural that this should be so, yet when we think that in the former case the boundary conditions are $u = 0$ both at $r = r_1$, and at $r = 0$, while in the latter case they are $u = 0$ at $r = r_1$, and $u = u_{max}$ at $r = 0$, it appears paradoxical that the flow should be the same in both cases. The explanation seems sufficiently curious to be worth a brief note.

If we seek for the place at which u has its maximum value in the concentric cylinder case, we have

$$\frac{du}{dr} = \frac{P}{4\eta l}\left(-2r_m + \frac{r_1^2 - r_0^2}{\log r_1/r_0}\frac{1}{r_m}\right)$$

or

$$r^2_m = \frac{r_1^2 - r_0^2}{2\log r_1/r_0},$$

where r_m is the distance from the axis for which u has its maximum value. If $r_0 = 0$, $\log r_1/r_0$ becomes infinite, and $r_m = 0$, so that the velocity is, in the limit, both zero and maximum at $r = 0$, and $\frac{du}{dr}$ is infinite. The velocity

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[1] See *e.g.* M. Brillouin, *Leçons sur la Viscosité*, p. 77.

gradient being infinite at $r = 0$, the velocity distribution is as shown in Fig. 1, if the points E, E are made to approach one another indefinitely. The velocity profile then becomes parabolic, as in the case of the open tube.
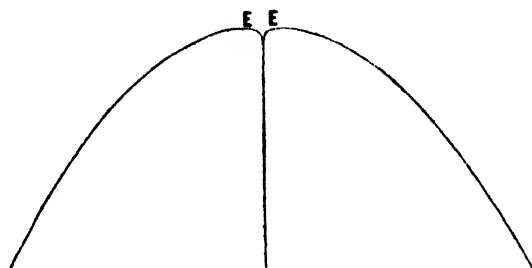
FIG. 1.—When $r_0 = 0$, E and E approach indefinitely, and the profile becomes parabolic.
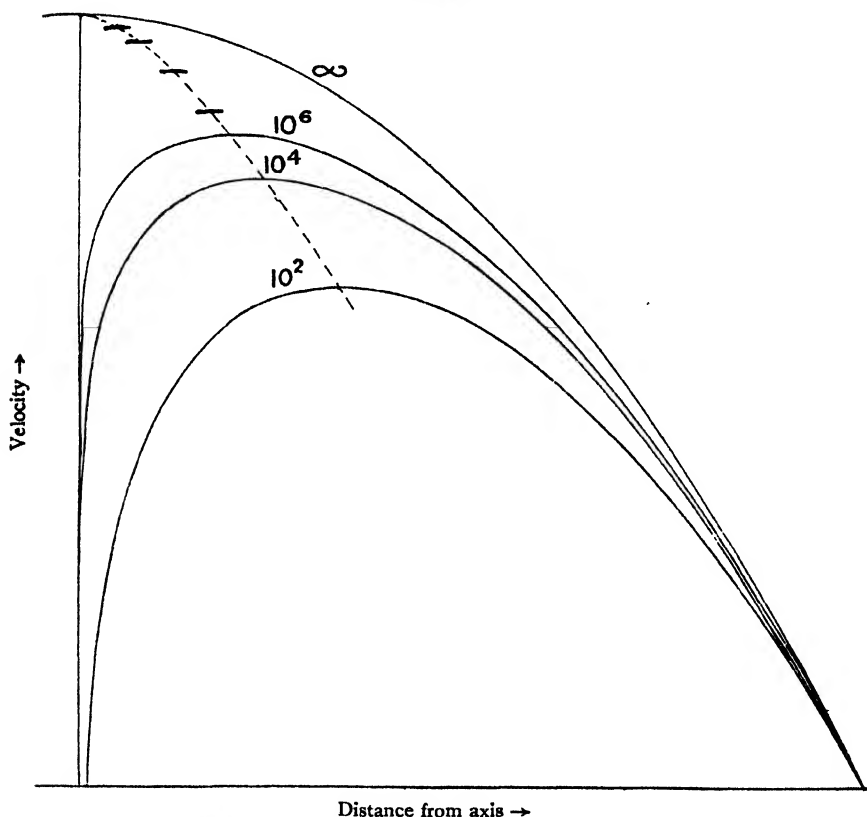
FIG 2.—Curves of velocity distribution for values $r_1/r_0 = \infty$, 10^6, 10^4, and 10^2. The broken line shows the position of maximum velocity. The short horizontal lines on it represent the maximum velocity for, reading from above, $r_1/r_0 = 10^{100}$, 10^{50}, 10^{16}, 10^8.

If, however, r_0 is finite, but nevertheless very small in comparison with r_1, it has a considerable effect on the flow. Suppose r_1 is 10,000 times r_0, or, to take possible figures, $r_0 = 0.001$ mm., $r_1 = 1$ cm.

Then
$$r_m = \frac{r_1}{\sqrt{2 \log_e 10^4}} = \frac{r_1}{\sqrt{18 \cdot 42}} = 0 \cdot 233 r_1,$$

and
$$V = V'\left(1 - \frac{1}{\log_e 10^4}\right) = 0 \cdot 891 \, V',$$

where V' is the delivery of a tube of radius r_1; or an axial wire of diameter one ten-thousandth that of the tube diminishes the flow by over 10 per cent. The following table shows, for various values of the ratio r_1/r_0, the values of r_m, the distance from the axis at which the velocity is maximum; and of u_m, the maximum velocity, and V, the delivery, in terms of the values V' and u_m' for the open tube. It will be seen that even if $r_1/r_0 = 10^{10}$ the flow is diminished by over 4 per cent.—not that such a ratio is of experimental interest!

r_1/r_0.	r_m/r_1.	V/V'.	u_m/u_m'.
10^2	0·329	0·783	0·650
10^4	·233	·891	·787
10^6	·190	·927	·844
10^{10}	·147	·957	·895

In Fig. 2 the velocity across the tube section is shown for the following values of r_1/r_0: infinity, 10^6, 10^4, 10^2. The broken line shows the position of the maximum velocity, and on this line are indicated the values of the maximum velocity for $r_1/r_0 = 10^{100}$, 10^{32}, 10^{16}, and 10^8, from which it will be seen that even if $r_1/r_0 = 10^{100}$ the position of the maximum velocity is still markedly displaced from the axis of the tube while the maximum velocity itself is markedly below the value for an open tube.

ON THE TECHNIQUE OF POLAROGRAPHIC MEASUREMENTS.

A CRITICISM OF MR. LLOYD'S PAPER.

By P. HERASYMENKO.

In a paper on the overvoltage at the dropping mercury cathode,[1] Mr. W. V. Lloyd comes to the conclusion that (i) contrary to the statement of P. Herasymenko the shape of the current voltage curves of hydrogen deposition varies with the change of the hydrogen ion concentration, and (ii) when applying a certain negative potential to the dropping cathode the current of hydrogen deposition increases very slowly with time. Hence, so Mr. Lloyd asserts, the method is unsuitable for hydrogen overvoltage measurements.

This last conclusion of Mr. Lloyd's was too hasty; on the basis of a few and uncritically performed experiments he has preferred to reject a method which has been thoroughly studied by a number of investigators

[1] *Trans. Faraday Soc.*, **26**, 12, 1930.

over a period covering approximately ten years of experience and has proved to give more reproducible results than any other method of investigation of polarisation phenomena.

Since the current at the dropping electrode fluctuates with the growth and dropping of the mercury, the galvanometer employed to record this current must have a sufficiently short period of swing in order that the deflection may adjust itself in due time. It was found that a galvanometer
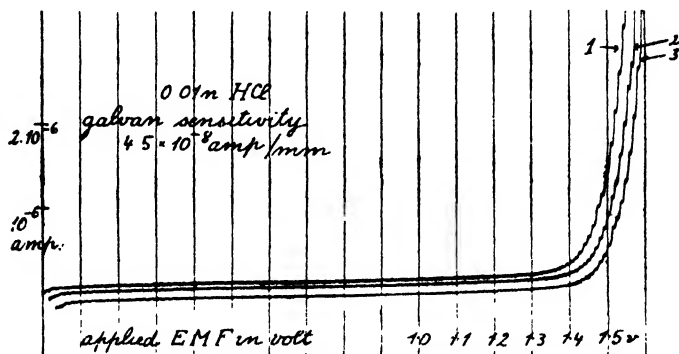
FIG. 1.

with the half-period of swing of about 4·5 seconds or less suits the purpose well enough when registering the curves automatically. Fig. 1 illustrates the exact reproducibility of the current-voltage curves obtained in acidic solution. Here the solution was 0·01 N hydrochloric acid from which air had been driven out by passing hydrogen through the solution for about four hours. The " dead beat " damping of the galvanometer has been adjusted by shunting the galvanometer through 1000 ohms and keeping in series 10,000 ohms. The instrument employed was a moving-coil ·mirror
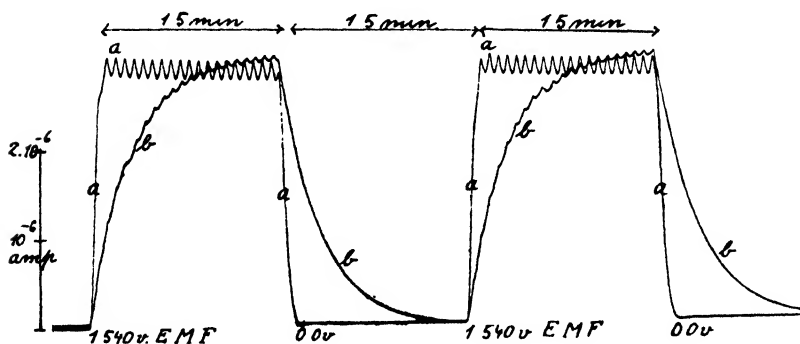
FIG. 2.

galvanometer of Hartmann-Braun, with 100-ohm internal resistance, sensitivity 4·5 × 10^{-9} amp./mm. and half-period of swing 4·5 seconds. The three curves are merely a repetition in the same solution, at intervals of 10 minutes, to show their coinciding course. The zero points of curves 2 and 3 were shifted to the right and below that of the first curve. Fig. 2 shows how the results of measurement can be influenced by neglecting the characteristics of the instrument employed. Here curve a was obtained

with a good damping of the galvanometer when at once a voltage of 1·540 volt was applied and kept constant for 1·5 minutes, after which interval the *E.M.F.* was disconnected ; this was repeated after 1·5 minutes.   Next the galvanometer was overdamped by using a small resistance (*viz.* 10-ohm) in the shunt, and adjusting approximately the same sensitivity ; thus curve *b* was obtained.   Here obviously the galvanometer deflexion was increasing but slowly reaching the final value in almost 2 minutes.   Such an unsuitable damping was most probably the cause of Mr. Lloyd's unsatisfactory results.

Instead of seeking the fault in his galvanometer Mr. Lloyd suggests that such a slow increase of the current is real, and he attributes to this an anomalous behaviour the mercury dropping electrode, concluding that Heyrovsky's method is unsuitable for the investigation of hydrogen overvoltage.   It is difficult to see how Mr. Lloyd could have imagined that a certain value of overvoltage is obtained after 2 minutes at a mercury cathode, the surface of which is renewed every two or three seconds.

Mr. Lloyd's statement that the shape of the current-voltage curves obtained with the dropping electrode varies with a change of electrolyte, is incorrect ; partly because he used a wrong method of measurement and partly because he did not take into account the current due to the continual charging of the double layer at the pulsating cathode surface.[2]

I thought it necessary to publish the preceding remarks, which are otherwise self-evident, since some authors seem to accept the unsatisfactory objections of Mr. Lloyd without giving them critical consideration.[3]

Plzeň, Czechoslovakia.

ON THE CALCULATION OF SURFACE TENSION FROM THE RISE OF LIQUIDS IN CAPILLARY TUBES.

By Alfred W. Porter, D.Sc., F.R.S., F.Inst.P.

Emeritus Professor of Physics in the University of London.

In the paper by the late Lord Rayleigh,[1] Poisson's equation for the ascent of liquids in capillary tubes was extended by an additional term so as to become

$$\beta^2 = \frac{r}{2}\left(h + \frac{r}{3}\right) - \frac{r^4}{6\beta^2}(\log 2 - \tfrac{1}{2}) + \frac{5}{36}\frac{r^6}{\beta^4}(3 \log 2 - 2) \quad . \quad (1)$$

for the case when the angle of contact is zero.   By successive approximations Rayleigh reduced this to

$$\beta^2 = \tfrac{1}{2}r[h + r/3 - 0\cdot1288\, r^2/h + 0\cdot1312\, r^3/h^2] \quad . \qquad . \quad (2)$$

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[2] The details with regard to this point were given in a paper by Mr. Slendyk and myself in *Z. physik. Chemie,* A **149**, 123, 1930.

[3] See H. J. S. Sand, *Trans. Faraday Soc.,* **26**, 19, 1930, and Newbery, *Proc. Amer. Electrochem. Soc., Preprint,* 1930.

[1] *Proc. Roy. Soc.,* A **92**, 184, 1915.

where β^2 is the capillary constant, surface tension/(g × density difference). The equation (1) is a true approximation up to and including the last term added. The final form (2) is, however, not very convergent and becomes divergent before the value $r/h = 1$ is attained. A more rapidly convergent series is obtained from the same original equation by taking as independent variable, not r/h, but $r/(h + r/3)$. In fact, $\frac{1}{2}r(h + r/3)$ is the first true approximation to β^2 and corresponds to taking the meniscus as being a hemisphere which it tends to become when the radius is very small compared with the elevation, h.
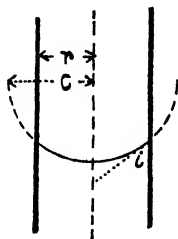
FIG. 1.

Writing (1) in the form which makes both sides pure numerics, and putting $\frac{1}{2}(h/r + 1/3) = \xi^2$ it becomes

$$\beta^2/r^2 = \xi^2\left\{1 - \frac{\cdot03219}{\xi^4} + \frac{\cdot01103}{\xi^6} - \frac{\cdot0010}{\xi^8} + \right\} \qquad . \qquad . \quad (3)$$

As an example take $r/h = 0\cdot3$ which is greater than is likely to occur in practice; the corresponding value of ξ^2 is $11/6$; whence

$$\beta^2/r^2 = \frac{11}{6}[1 - 0\cdot00958 + 0\cdot00251 - 0\cdot0001] = 1\cdot8187.$$

This differs by only 5 in 18,000 from the value determined by means of the tables of Bashforth and Adams, *viz.*, $1\cdot8182$. The value calculated by (2) is $1\cdot8199$ which differs by about 1 in 1000 from the tabular value, the contributions of the several terms being indicated by the equation

$$1\cdot8199 = \frac{10}{6}(1 + 0\cdot1 - 0\cdot01159 + 0\cdot003542).$$

When the angle of contact is not zero the matter becomes much more complicated. Rayleigh again led the way by showing that the equation to the meniscus is

$$y = c - \sqrt{c^2 - x^2} + \frac{c^3}{3\beta^2}\left(1 - \frac{c^2}{\beta^2}\right)\log\frac{c + \sqrt{c^2 - x^2}}{c}$$

$$+ \frac{c^5}{6\beta^4}\left[\frac{\sqrt{c^2 - x^2} - c}{c} + \frac{c}{\sqrt{c^2 - x^2}}\log\frac{c + \sqrt{c^2 - x^2}}{c}\right] + constant. \quad (4)$$

The value of c is the radius at which the meniscus becomes vertical. He restricted himself, however, to the case for which the angle of contact is zero. If its value is i for a tube of radius r we can consider the actual meniscus extended in accordance with the law of capillary elevation until it becomes vertical at radius c, as in Fig. 1, and the above equation then applies.

By differentiation and insertion of $x = r$ one obtains

$$\cot i = -\frac{r}{\sqrt{c^2 - r^2}}\left[\begin{array}{c} 1 - \frac{c^3}{3\beta^2}\left(1 - \frac{c^2}{\beta^2}\right)\frac{1}{c + \sqrt{c^2 - r^2}} \\ + \frac{c^5}{6\beta^4}\left(-\frac{1}{c} + \frac{c}{(c^2 - r^2)}\log\frac{c + \sqrt{c^2 - r^2}}{c}\right. \\ \left. - \frac{c}{\sqrt{c^2 - r^2}(c + \sqrt{c^2 - r^2})}\right) \end{array}\right] \quad (5)$$

This equation can be simplified by substituting $r/c \equiv \cos\phi$ (exactly) so that ϕ is nearly equal to i. By squaring and rearranging it then becomes

$$c^2 = \frac{r^2}{\cos^2 i}\left[1 - \frac{c^2}{3\beta^2}\frac{\sin^2 i}{1+\sin\phi} + \frac{c^4}{3\beta^4}\left\{ \frac{\sin^2 i}{1+\sin\phi}\left(1 - \sin\phi - \frac{1}{\sin\phi} + \frac{1}{3}\frac{1}{1+\sin\phi}\right) + \frac{\sin^2 i}{\sin^2\phi}\log(1+\sin\phi)\right\}\right] \quad (6)$$
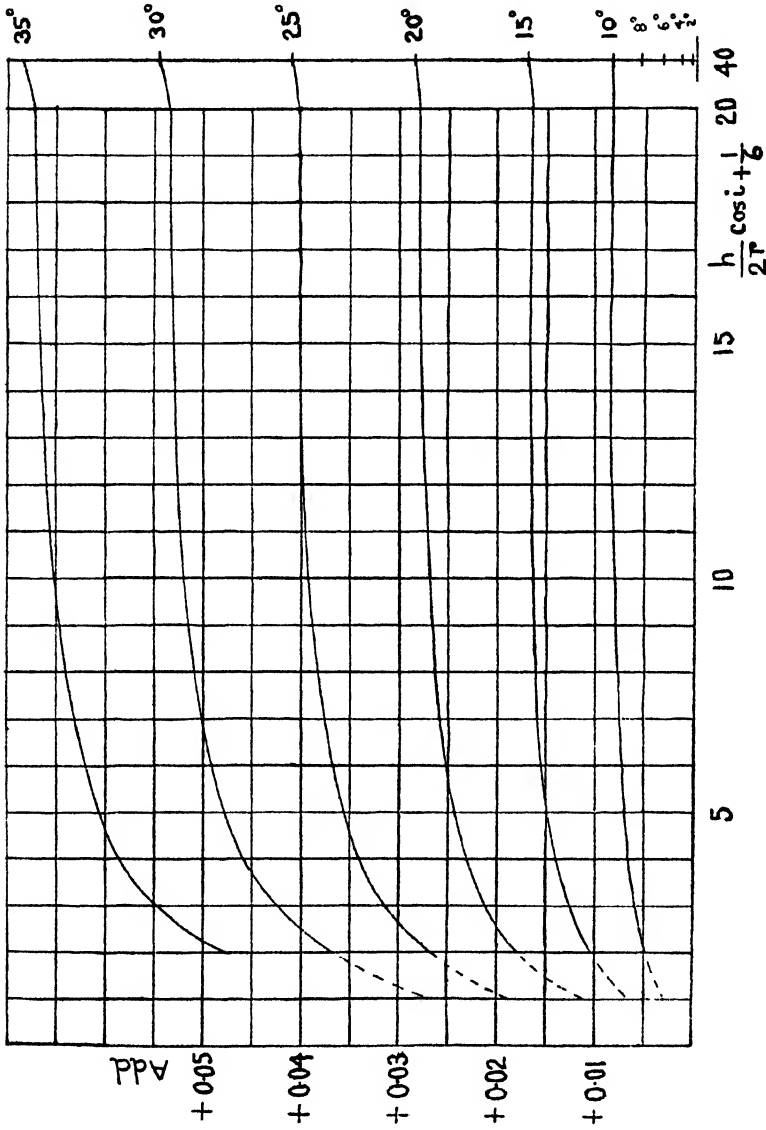
Diagram A.

Now $\dfrac{\beta^2}{c^2} = \xi_c^2\left\{1 - \dfrac{\cdot 03219}{\xi_c^4} \text{ etc.}\right\}$ by (3); and by putting $\phi = i$ in the small terms only we obtain a relation between r, c, and i. Calling this

Diagram B.
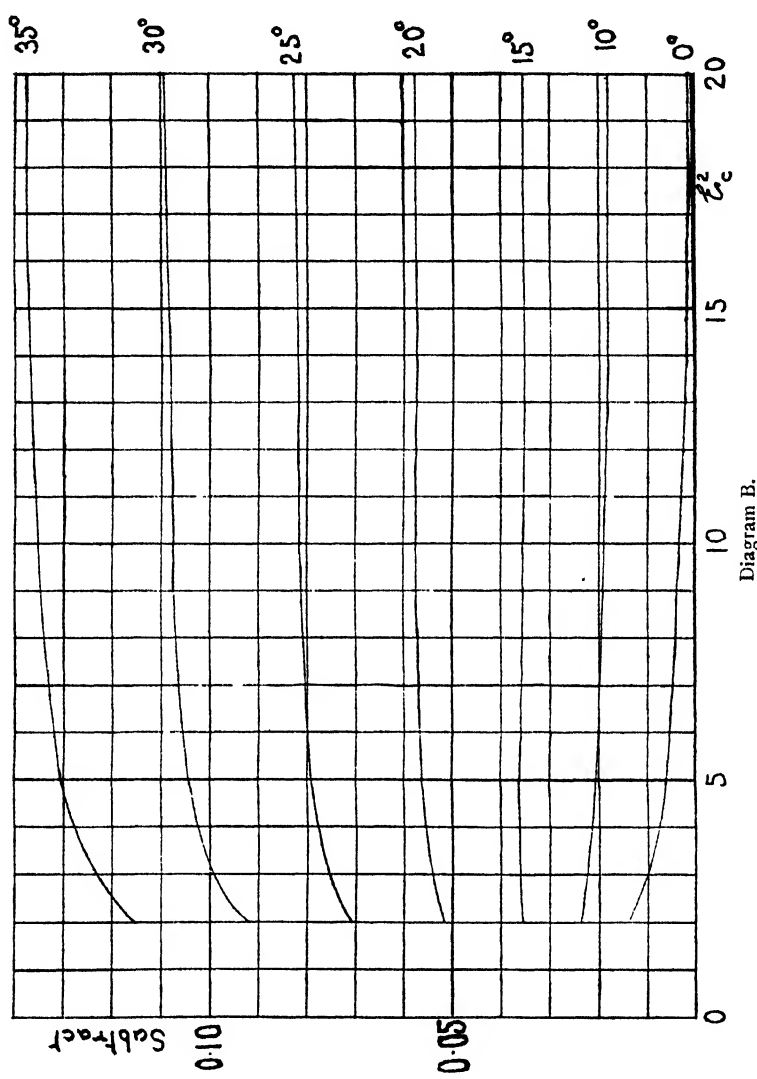
relation $c^2 = \dfrac{r^2}{\cos^2 i}(1 - \lambda)^2$ where λ is small compared with unity, it follows that

$$\frac{h\cos i}{2r} = (\xi_c^2 - \tfrac{1}{8})(1 - \lambda),$$

and $\dfrac{\beta^2 \cos^2 i}{r^2} = \dfrac{\beta^2}{c^2}(1 - \lambda)^2 = \xi_c^2\left(1 - \dfrac{\cdot 03219}{\xi_c^4} + \dfrac{\cdot 01103}{\xi_c^6} - \right)(1 - \lambda)^2$

whence $\dfrac{\beta^2}{h^2} = \xi_c^2 \dfrac{\left(1 - \dfrac{\cdot 03219}{\xi_c^4} + \dfrac{\cdot 01103}{\xi_c^6} - \right)}{4(\xi_c^2 - \frac{1}{6})^2}$ . . . . . (7)
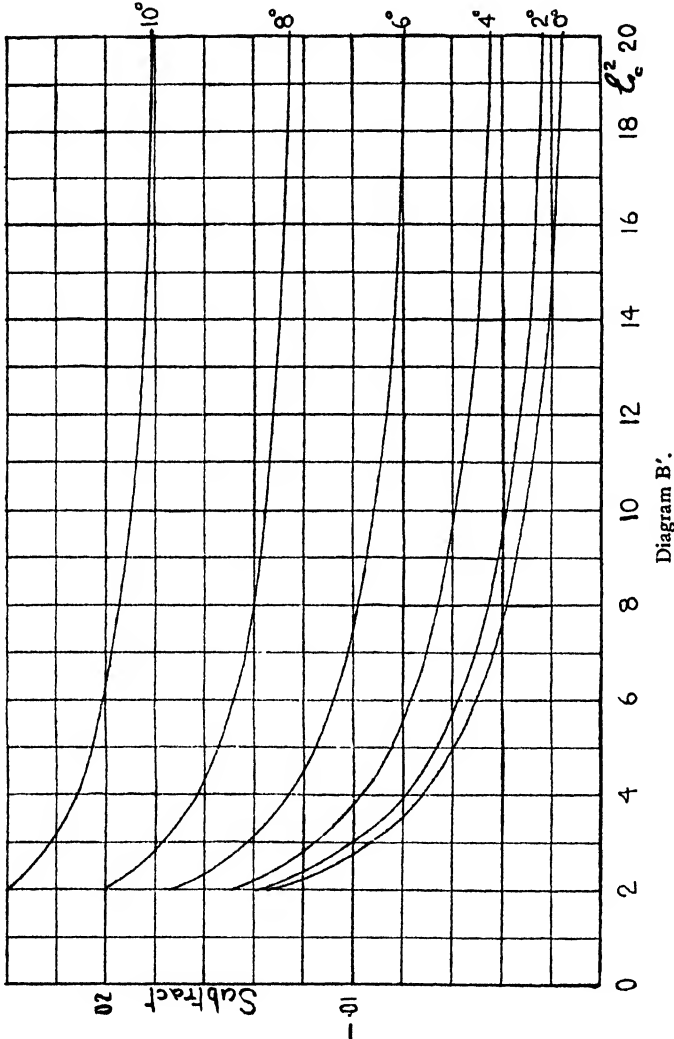
Diagram B'.

The solution of the problem for β^2 when the experimental data are h, r, and i is effected in two stages, the first of which determines the intermediary parameter ξ_c^2.

A. To find ξ_c^2.—On diagram A each abscissa represents a value of $\dfrac{h \cos i}{2r} + \dfrac{1}{6}$ which can be calculated from the experimental data. The

corresponding ordinate on the appropriate curve gives the small quantity which added to the abscissa gives in turn the desired value of ξ_0^2.

B. To find β^2.—Two methods are available :—

(a) β^2/h^2 can be calculated from ξ_c^2 by means of (7); and thence β^2 ; or alternatively,

(b) $(\beta^2 \cos^2 i)/r^2$ can be determined by means of diagram B (or B' for small angles of contact.) Any abscissa on B (or B') is a value of ξ_c^2. The corresponding ordinate of the appropriate curve gives the small quantity which *subtracted from* ξ_c^2 gives the corresponding value of $(\beta^2 \cos^2 i)/r^2$ from which β^2 is to be calculated.

Example :—Let $r = 0\cdot 1$ cm., $h = 3$ cms., and $i = 30°$. Here $\dfrac{h \cos i}{2r} + \dfrac{1}{6} = 13\cdot 157$; the correction obtained from A is about $0\cdot 0526$ making $\xi_c^2 = 13\cdot 210$. Diagram B indicates a subtractive correction $0\cdot 1082$ which leads finally to the value $\beta^2 = 0\cdot 17469$. Calculation by method B (a) gives the same result to five significant figures. Whether the figures have real significance depends, of course, upon the accuracy of the experimental measurements which provide the fundamental data. These can seldom be guaranteed to more than three significant figures.

It must be pointed out that the corrections are valid for capillary depression as well as for capillary rise. This is to be inferred from the facts that (a) h is always associated with $\cos i$ and both change sign together, (b) β^2 is associated with $\cos^2 i$ which does not change sign, (c) also $\sin i$ does not change sign. The simplest rule is to consider both rise and depression as positive, and to let i denote the *acute* angle of contact.

The present paper carries the question of the calculation of the capillary constant as far as the existing theoretical specification of the capillary surface for narrow tubes. It would appear to be quite safe provided $\dfrac{\beta \cos i}{r}$ is not less than unity. The behaviour of a liquid in wide tubes requires specific examination.

The diagrams only indicate small differences ; hence it has been possible to construct them with very open scales.

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THE MEASUREMENT OF GLASS ELECTRODE POTENTIALS.

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Introduction.

It is essential in measuring glass electrode potentials to use an electrostatic method, *i.e.* one in which the current passing through the cell is so small that its effect is negligible. The quadrant electrometer has been much used, particularly in the Lindemann form (Kerridge, 1926). Although this instrument is satisfactory in many ways, a certain amount

of care and patience is demanded in order to maintain its sensitivity at the maximum value, which does not in our experience, under the best conditions, exceed 0·4 micrometer eyepiece scale divisions per millivolt. This corresponds to an accuracy of $\pm$ 0·3 mv. ($\pm$ 0·005 p_H), and requires the use of a special switch.* [Mirsky and Anson (1929).] Among other methods of measurement may be mentioned a condenser and ballistic galvanometer one used by Morton (1930), and more recently by Dole (1931). Although this method has been proved to be sound, an almost prohibitive amount of time has to be spent over each reading. Finally, thermionic valve potentiometers employing both three- and four-electrode valves have recently been developed into electrostatic instruments.

Theoretical.

The most useful form of valve electrometer employs a null point method of measurement. The grid is brought to a certain fixed potential ; a system consisting of the unknown potential, together with an opposed potentiometer is then inserted in the grid circuit, and the potentiometer is adjusted to bring the grid back to its original potential, as shown by observation of the anode current. The potentiometer reading is then equal and opposite to the unknown potential. Now, in general, a grid current i_g, the resultant of leakage currents, grid electron flow, and positive gas ion migrations, flows between the filament and grid of a valve : when plotted against grid potential it gives a curve of the type
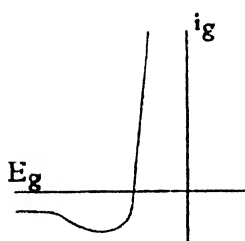
FIG. 1.
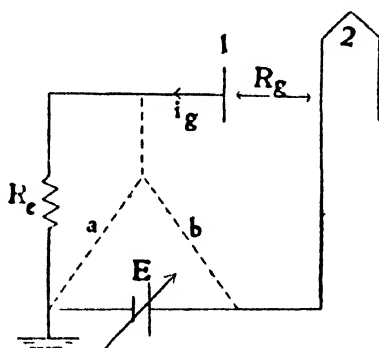
FIG. 2.—1 Grid ; 2 Filament.

shown in Fig. 1. i_g becomes zero and changes sign at a potential which is that assumed by the grid on open circuit, and is often called the " floating grid potential." If there be an external resistance R_e in the grid circuit, there will be a fall of potential across it equal to $i_g R_e$, which value represents a discrepancy between a potential applied to the grid circuit and that which actually biases the valve, and is also the error introduced into the null method by the flow of grid current. Under these conditions the sensitivity is also decreased, for (with the conventional notation indicated in Fig. 2) the potential applied to the grid is not E but

$$E' = \frac{R_g}{R_g + R_e} \cdot E.$$

* Instead of the Mirsky and Anson switch, a glass and metal switch of the type described later in this paper may with advantage be used in conjunction with the Lindemann electrometer. It is smooth in action, simpler to construct, and easier to keep clean.

If i_p be the plate current, the mutual conductance is $G = \frac{\partial i_p}{\partial E}$ without

the resistance, and $G' = \frac{\partial i_p}{\partial E'}$ with the resistance.

Hence
$$\frac{G'}{G} = \frac{\partial E}{\partial E'} = \frac{R_g}{R_g + R_e}.$$

This result is represented graphically in Fig. 3, 1 being the curve without resistance, 2 that with resistance. A family of curves passes through the point F, each corresponding to a given resistance, the slope of each measuring the mutual conductance. F corresponds to the floating grid potential.

In the earlier circuits proposed (Stadie, 1929; Partridge, 1929; Elder, 1929; Elder and Wright, 1928; Schwarzenbach, 1930) grid current was allowed to flow; but recently two methods have been used to reduce i_g to a very small value. Voegtlin, de Eds, Kahler, 1929, 1930; Müller, 1930; Fosbinder, 1930; and Dubois, 1930, work at the floating grid potential. The discrepancy is thus removed, but the sensitivity is still impaired by high resistances. Thus Fosbinder needs to use electrodes of less than $25\,\Omega$ to preserve an accuracy of 0·1 mv.; Dubois by applying a negative screen-grid potential works with a very small anode current, and his sensitivity is less affected by high resistances, but his maximum sensitivity is much lower than Fosbinder's. The other method was described by Harrison (1930), who employs a valve of unusual design called the electrometer triode. In this the placing of the filament between the grid and the plate and use of very high vacua reduce the grid current, when the grid bias is more negative than the floating grid potential, to a value no greater than that achieved by Fosbinder and Dubois in working at the floating grid potential. The mutual conductance of this valve is low, but is unaffected except by enormous resistances in the grid circuit. Harrison's apparatus is extremely simple and was, in fact, designed for works use. In those of Dubois and of Fosbinder the grid has to be brought to the floating grid potential before each reading; this is an additional control, and, moreover, demands elaborate shielding. Harrison only aimed at an accuracy of $\pm$ 1 mv., and did not check his apparatus against any other electrometer. In the present paper is described a development of his apparatus which attains an accuracy of 0·1 mv., and is suitable for the most precise measurements of glass electrode potentials. The chief modifications consist of the use of a more sensitive galvanometer and the introduction of a special switch.
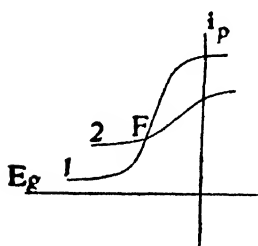
F G. 3.

The Valve Electrometer: Practical Details.

The galvanometer used had a sensitivity of 270 mm./microampère; with − 2 volts on the grid and 4 volts on the anode, a sensitivity of 7 mm. per millivolt was obtained, and with the same grid bias and 6 volts on the anode 12 mm. per mv. It was feared that with the increased sensitivity variation in the anode current might produce a drift of the galvanometer needle, which would obscure the accuracy of the reading; but it was found that, provided the batteries were well charged and the

connections tight, a state of equilibrium was reached in about fifteen minutes after switching on, after which the drift was negligible (seldom greater than 2 mm. per minute, and usually less). Dry cells, storage cells or H.T. accumulators may be used indiscriminately for anode battery and grid bias. We have used a pair of standard Weston cells for the latter, but this possesses no advantage. Harrison balanced out the steady anode current through the galvanometer by passing through it and a high resistance a current from the filament battery. The resistance of a sensitive galvanometer, however, may be comparable with this compensating resistance, in which case some of the sensitivity of the apparatus is lost. It is then best to use a separate battery * for this compensation, whose E.M.F. is high enough to allow the use of a compensating resistance large compared with the galvanometer resistance.

The Switch.

In Harrison's circuit (Fig. 4a) it will be seen that the glass electrode and potentiometer form a closed circuit. This is very undesirable, as if the potentiometer is out of balance a current will flow through the glass electrode which may produce significant polarisation. In order to test the magnitude of this effect, different potentials were applied for stated times by upsetting the potentiometer balance, and the glass electrode potential measured before and after with the improved apparatus described below. The following results are typical :—

| Reading (mv.) | 105·0 | 105·0 | 105·0† | 111 | 109·1 | 108·1 | 107·1 |
| Time | 0 | 2′ | 4′ | 5′25″ | 5′35″ | 6′2″ | 6′33″ |

| Reading (mv.) | 106·0 | 105·0 | 105·0 |
| Time | 11′ | 34′ | 40′ |

† 300 mv. applied here for 1 minute.

| Reading (mv.) | 82·2† | 82·75 | 82·5 | 82·2 |
| Time | 0 | 40″ | 70″ | 100″ |

† 100 mv. applied here for 30 seconds.

(a)   (b)   (c)
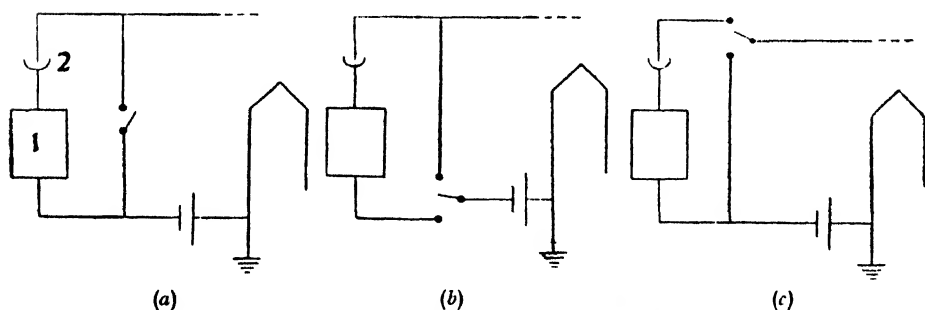
FIG. 4.—1 Potentiometer; 2 Glass electrode.

The second series was obtained by using the Harrison switch with a glass electrode which was less sensitive to polarisation effect. These electrodes were made as recommended by MacInnes and Dole (1929, 1930). Such potential differences as above might easily be applied to the electrode with Harrison's circuit during a series of determinations ranging from acid to alkaline solutions.

There are two possible ways of overcoming this difficulty by two-way switches (b and c, Fig. 4). In either case, the second path must be made

* Shown by broken lines in Fig. 6.

before the first is broken, or the grid will tend to rise towards the floating grid potential due to the breaking of the grid circuit. The switch *b* would be the more convenient, as the highly-insulated grid is not connected to the moving part ; but we found that its use was accompanied by a most undesirable kick of the galvanometer needle, which returned only slowly to its final deflection. This appeared to be due to the glass electrode acting as a condenser, for it was not obtained with a resistance of equal magnitude in place of the electrode. A switch of the type *c* has, however, proved perfectly satisfactory. An all-glass switch sliding in brass clips proved to be unsuitable, as it caused a large kick with a high resistance in the grid circuit, possibly due to the development of frictional charges which leaked away slowly. The final switch, which was the only really satisfactory one constructed, is shown in Fig. 5. At the end of an insulated spindle, two phosphor bronze strips, A and B, fixed radially at a small angle to each other, move between two copper contacts,

FIG. 5.—1 Grid; 2 Pyrex tube; 3 Glass electrode; 4 Grid bias minus. The lead below D goes to the grid.

C and D, one of which is connected to the glass electrode and one to grid bias minus. In the mid position, the two strips press against their nearest contacts. If the spindle be rotated slightly one way, one strip moves away from one contact, leaving the other strip pressing against the other contact. This is made possible by the flexibility of the strips. The two strips are connected to the grid, so that the grid can be connected to G.B. minus, to the glass electrode, or to both, according to the degree of rotation of the spindle. A spring attached to the spindle keeps it normally so that the grid is connected to G.B. minus. The construction is as follows : The strips are fixed by sealing wax to a Pyrex glass tube, which is fixed by a cement (" Museum jar cement " was used) to a metal spindle passing through suitable bearings in the side of the box. A knob outside the box rotates the switch. Good contact was ensured by lightly smearing the cleaned metal with vaseline. The spindle is connected to G.B. minus. The switch can be made very easily from Mecanno parts.

Construction.

The complete apparatus is shown in Fig. 6. The jacks A and B enable the galvanometer to be used either in the anode circuit or to standardise the potentiometer : when the plug is removed from jack B the " galvanometer " terminals of the potentiometer are automatically short-circuited. The valve, its concomitant resistances, and the switch are mounted in a box. The glass electrode apparatus is placed in an air-bath, whose sides are lined with earthed sheet zinc, covered with asbestos, and which has two large windows covered with earthed net and two hand-holes with sliding doors. For use with low resistance electrodes

of the MacInnes and Dole type (up to about 60Ω in resistance) the only shielding necessary for the valve box is earthed tinfoil pasted on the lid. For Kerridge electrodes (500Ω and higher) more shielding is necessary. We line the whole of the inside of the box with earthed foil, and place an earthed sheet of perforated zinc between the valve and the resistances. The lead between the valve box and air bath is surrounded by an earthed cylinder. We find that to bring a glass rod rubbed with silk near the vital points is a dramatic test of the efficiency of the shielding. The only parts of the circuit requiring great care in the insulation are the connections from the grid and glass electrode to the switch. To carry the latter we use two " Orca " terminals (as supplied by the Cambridge Instrument Company for their glass electrode outfit), one in the valve
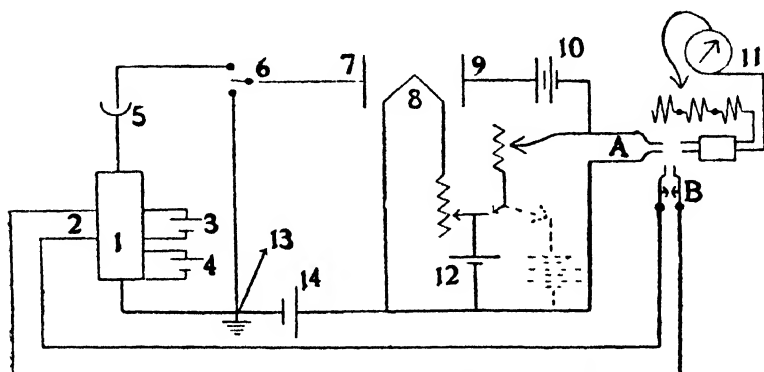
Fig. 6.—1 Potentiometer; 2 Leads to G.T.; 3 St.C.; 4 P.C.; 5 Glass electrode; 6 Switch; 7 Grid; 8 Filament; 9 Anode; 10 Anode battery; 11 Galvanometer; 12 Filament battery; 13 Shielding; 14 Grid battery.

box and one in the air-bath. It is important that the shielding should be connected, and the earth connection made, to grid bias minus, and not to grid bias plus, as was done by Harrison. The reason for this is that if there be an electrical leak to the shielding from the insulated grid connections when the shielding is connected to grid bias plus, current will flow through a circuit formed through the electrode and the grid battery; whereas if the shielding be connected to grid bias minus the current will in general be very much smaller, for the applied potential will not be the full $E.M.F.$ of the grid battery, but a fraction of it which depends on the relative values of the leakage resistances between the insulated part of the grid circuit, and the positive and negative poles of the grid battery. (See paths a and b, Fig. 2.) This we have demonstrated experimentally.

Methods of Testing.

The fundamental test of the apparatus is, of course, to observe whether the value of a source of potential, as measured by it, is altered by the introduction of a resistance into the grid circuit. The discrepancy, divided by the value of the resistance, gives the current flowing through the resistance. If a grid current correspond to a biasing potential less negative than the floating grid potential, the discrepancy will be of one sense; if it correspond to a potential more negative than the floating potential the discrepancy will be of the opposite sign. A leak from the grid lead to earth (which may be a leak over the surface of the valve)

will cause a discrepancy of the latter sense. The test is made by putting the high resistance in the air-bath and connecting it (preferably with air insulation) between the potentiometer lead and Orca terminal. A simple and permanent testing resistance is made by connecting four or five 10Ω grid leak by grid leak clips soldered together in pairs. An illustrative series is as follows :—

Potential of standard cell, no resistance in series					= 1018·0 mv.
,,	,,	,,	40Ω	,,	(G.B. = − 2 volts) = 1030 ,,
,,	,,	,,	40Ω	,,	(,, = − 3 ,,) = 1018·0 ,,

Since the grid bias must be more negative than the floating grid potential, this affords a method of choosing a suitable value for it. Another method of determining the floating grid potential consists in adjusting a potentiometer connected in place of the grid battery until the anode current remains the same whether the grid is connected to this potentiometer or is floating. Harrison invariably uses a $1\frac{1}{2}$-volt grid battery ; but we find (as above) that even two volts are not enough for some valves ; however, with most valves two volts are adequate.

For more stringent tests it is necessary to construct higher resistances. We have been unable to get satisfactory results from the glass and mercury resistance of Dubois (1930), but we have made excellent resistances in the following manner : The ends of a stick of sealing wax are heavily leaded with a very soft pencil (3B), and a broad pencil line is drawn between these along the line of the stick with a very hard pencil (2H). Brass brackets are screwed down at the ends and the connections made to these. The magnitude of the resistance is, of course, governed by the depth of the pencil line, which is adjusted by lightly rubbing with cotton wool ; and in this way we have made resistances of from $500\,\Omega$ to $16,000\,\Omega$ resistance. They appeared to remain constant and to give no evidence of contact potentials or polarisation. One whose resistance, determined by connecting it in series with the galvanometer and 80 volts, was found to be $1\cdot6 \pm 0\cdot2 \times 10^{10}$ ohms, was connected in the grid circuit in series with the potentiometer and the discrepancy measured. Half an hour after the glass below the grid terminal had been cleaned with absolute alcohol the necessary potentiometer reading was $0\cdot35 \pm 0\cdot05$ millivolt, corresponding to a grid current of 2×10^{-14} ampères ; and when the surface was further dried by holding near it a mass of hot metal the current fell to $1\cdot25 \times 10^{-14}$ ampères. The insulation resistance between grid and filament was, therefore, under these conditions $1\cdot6 \times 10^{14}$ ohms. This is, of course, far in excess of glass electrode requirements, and further, there would only be a 1 per cent. (negligible) loss of sensitivity with one million megohms in the grid circuit.

There are two further forms of leak for which tests should be made, and these occur in the glass electrode apparatus itself. An electrical leak around the membrane into the solution will cause its apparent potential to be $\dfrac{re}{R + r}$, where e is the true potential, and R the resistance of the membrane, and r the leakage resistance. This apparent potential will be registered by both Lindemann and valve electrometers. The only way of demonstrating that the leakage around the membrane is negligible is to establish that the hydrogen electrode function of the electrode is perfect over a reasonably wide range. This may be done by determining the potentials given with at least two standard buffer

solutions. These buffers must either be ones made from specially purified chemicals, or their p_H values must have been determined by the hydrogen electrode. The second type of leak is that from the side of the membrane connected to the grid. It may be seen by inspection of Fig. 2 that this leak if it pass to earth, will not affect the glass electrode potential, but if the leakage resistance to grid bias plus (path *b*, Fig. 2) is not very large compared with that to grid bias minus (path *a*, Fig. 2) a current may pass through the membrane from the grid battery when the valve potentiometer is used. Such a leak might easily occur with the Kerridge form of electrode. Its effect will clearly be shown up by measuring the potential with both valve and Lindemann electrometers, for with the latter there is no source of potential other than the membrane and potentiometer. The following test was done with a MacInnes and Dole electrode, resistance 54 Ω.

Sensitivity of Lindemann = 0·4 scale divisions/mv.
     ,,   ,, valve   = 6·5 mm/mv.

Solution.	Valve.	Lindemann.	Valve.
	mv.	mv.	mv.
Phosphate buffer.	140·0 ± 0·05	140·0 ± 0·3	140·0 ± 0·05
Phthalate ,,	— 85·3	— 85·7	— 85·4
HCl N/10	— 256·0	— 256·0	— 256·0

The determination on the valve was repeated after that on Lindemann to ensure that the glass electrode potential had not changed. In this connection it is interesting to note that in the changing-over process it was not permissible to touch the lead to the side of the membrane remote from earth, for this temporarily disturbed the membrane potential by more than 10 millivolts. This is further evidence for the ease of polarisation of glass electrodes. A similar satisfactory agreement between valve and Lindemann was obtained with a Kerridge electrode of 700 Ω resistance, both when the grid was connected to the calomel cell dipping into the cup and when it was connected to the cell dipping into the fluid on the other side of the membrane. We had considered it possible that insulation from earth was not equal on the two sides of the membrane.

The methods of testing have been discussed in some detail because those described by previous authors have been quite inadequate ; in some cases it will be seen on examination that they afford no information whatsoever.

In the above work we have used the electrometer triode manufactured by Messrs. Philips Lamps, Ltd., and also an experimental valve of the same type kindly lent to us by the Director of the Research Laboratories of the General Electric Company. In the latter valve the grid connection is carried to a terminal at the end of a tube of special resistance glass fused on top of the bulb. This valve was used for the grid current measurements.

The Preparation of Glass Electrodes.

It has been the practice until recently to use some form of bulb electrode (Kerridge 1926, Hughes 1928, Voegtlin, de Eds, Kahler 1930, Morton 1930, Harrison 1930), but the electrodes described by MacInness and Dole * (1929) are, in our opinion, the most generally useful as they

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* These electrodes are prepared as follows : a thin bulb is blown from the special glass so that interference colours are visible. The end of a piece of ordinary glass tubing is then made just red hot and applied at right angles to the surface of the bulb, so that the end of the tube is closed by a fine membrane.

are easier to prepare, the thickness of the glass is under better control, and they may be used for very small quantities of fluid. The composition of the glass is of great importance, for we were unable to prepare them satisfactorily from glasses which were quite suitable for bulb electrodes, for example, that recommended by Hughes (1928). A commercial glass specially made according to the specification of MacInnes and Dole * (although not strictly free from aluminium and potassium) proved quite satisfactory.

The electrodes are easily prepared with a little practice, but it is advisable to prepare a number at one time for some of those which appear perfect have minute holes, or other faults, which can only be demonstrated by an actual test on buffer solutions. They are more durable if made rather smaller than is recommended by MacInnes and Dole—say from 2 to 3 mm. diameter—and apparently quite as satisfactory. Such electrodes may be handled without undue respect when dry, but are rather easily broken when full of water. The method of suspension described below is a great help in diminishing breakages.

They should be stored overnight in the phthalate-KCl-calomel solution (see below), and each one should be tested before use on two solutions of known p_H, not only to exclude minute holes, but also because large and erratic asymmetric potentials are sometimes formed or the change of potential may be considerably less than that corresponding to the p_H difference. This, of course, applies to any glass electrode. It may be due to a minute air bubble just above the membrane, which is difficult to see, but otherwise the electrode must be discarded. Any two standard buffer solutions whose p_H values do not lie too close together may be used for this purpose. Of course, the electrode must be so standardised at least once daily. The electrode should not be left dry after use for any considerable period, or an asymmetry potential of several millivolts may develop ; we always leave the electrodes dipping in water.

The Arrangement of Half Cells.

The cells which we use in the measurement are as follows :—

Hg.	HgCl KCl 0·1 N Potassium hydrogen phthalate $M/20$	Glass membrane	Unknown solution.	HgCl KCl 3·5N	Hg.

This system shares with those of Mirsky and Anson (1929) and MacInnes and Dole (1930) the advantage of having only one liquid junction and, in addition, the p_H of the solution on the left of the membrane is kept more rigidly constant by the presence of the pthalate buffer. In our experience this does not affect the stability of the calomel cell, while the calomel itself prevents the growth of moulds in the phthalate so that it keeps indefinitely. The design of the apparatus depends upon the degree of accuracy required and the amount of material available.

In work at room temperature, that is, without thermostat, an accuracy of $\pm$ 0·01 p_H is probably all that can be hoped for. For very small quantities the apparatus described by MacInnes and Dole (1929a) can hardly be improved, but where larger amounts are available that shown in Fig. 7 will be found very convenient.

* SiO_2 72 per cent., Na_2O 22 per cent., CaO 6 per cent.

The calomel cell vessel is a modification of that described by Ellis (1916), the special feature of which is that after closing tap A it may be shaken to hasten equilibrium. There is no possibility of fouling the mercury-platinum contact with calomel (a frequent source of trouble with calomel cells) and the cell may even be remade without disturbing this contact. A further advantage is the small heat capacity which allows the cell to arrive rapidly at the temperature of an air bath, although for the same reason draughts should be avoided when working at room temperature. The glass electrode is suspended by means of an ordinary rubber teat B, of which most of the bulb has been cut away to leave two strips. Both of these are bored with small holes and slip easily on to the two pins C.C., so that the electrode hangs freely from the rubber sleeve D. The electrode should be placed in position empty and dry on the outside, and then filled *in situ* from the reservoir E, care being taken to dislodge air bubbles from the membrane by gently tapping with the finger. A drop of liquid paraffin is finally added to prevent evaporation ; it must not touch the electrode surface from which it is difficult to remove. This device permits the rapid changing of electrodes and minimises breakages by acting as a shock-absorber.
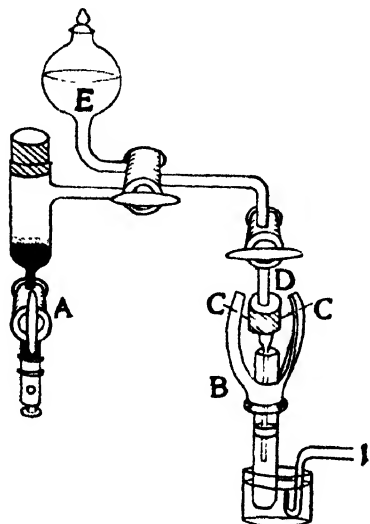
FIG. 7.—1 To 3·5 N KCl-Calomel cell.

The intermediate vessel F holds about 2 c.c. It may with advantage be mounted on a rotating table for work with viscous solutions (see below).

The liquid junction between the 3·5 N KCl, and the unknown solution is formed at the end of a fine capillary tube as shown. It is quite essential for this tube to be turned up for about 5 mm., otherwise gross mixing occurs between the solution and the heavier KCl. This method of making the junction gives very little contamination and a remarkably steady potential, even with hydrochloric acid solutions,* being free from the drifts of potential which have been observed, even in phosphate solutions, with glass caps recommended by Kerridge (Maclagan, 1929).

More Accurate Measurements.

If a greater accuracy than ± 0·01 p_H be desired, accurate temperature control and a more reproducible form of liquid junction are necessary. Further, if an air-bath is to be used, an open vessel is not permissible on account of evaporation and cooling. It may be mentioned that other essentials such as calomel cells which do not fluctuate and a reliable p_H standard are also of the greatest importance where the highest accuracy is sought. In this connection the remarkable results obtained by Livingston,

* Although this junction gives quite a steady potential with HCl solutions, we have some evidence to show that it is not quite the same potential as that given by more orthodox methods. An error of about 1 millivolt occurs with $N/10$ HCl which should not, therefore, be used with this junction where this error is significant.

Morgan and Campbell (1931) on the quinhydrone electrode suggest that it may be an advantage to use this as a half cell in place of the calomel cell. These workers obtained a reproducibility of 1/100 millivolt without any special difficulty as a result of certain improvements in the preparation and cleaning of the platinum electrodes.

The whole subject of ultimate p_H standards for use with glass electrodes is in a most unsatisfactory state, as will be seen from the large number of different standards in use (*cf.* Clark, 1928, p. 478, l. 3), and demands careful consideration. Further work is urgently needed on this subject.

With regard to the liquid junction potential, it has been shown by one of us (Maclagan, 1929) that the most important condition for reproducibility and stability of liquid junctions is that the junction be formed within a tube of not too small a diameter, and not at its end ; the suggestion was also made that the final reading and not the initial one should be taken. Very similar recommendations are made independently by Guggenheim (1930), who was able to show theoretically that the advantage lay in the " cylindrical symmetry " of junctions inside tubes, which was not obtained by those at the end. More recently, Unmack and Guggenheim (1930) also take the final reading for junctions inside vertical tubes. On the other hand, in the Clark (1915) hydrogen electrode the junction is formed inside a *sloping* tube, and there is no evidence that this will give exactly the same result. In this connection we may mention the observation of Biers (1927) that the Clark junction differs from the flowing junction by 50· mv. with N HCl/sat. KCl. Presumably alterations in the slope of the tube will not affect the potential with solutions in the neutral range.

These considerations will suggest the design of apparatus to be used in any particular case ; and that shown in Fig. 8 is only to be regarded as an example. It was designed for use with blood or other body fluids in which the carbon dioxide tension is of paramount importance. It is filled by applying a syringe to the rubber tube A and opening the tap B. Owing to the slight tilt all the air is driven out. The tap is closed before withdrawing the syringe. The liquid junction is formed inside the tube C by squeezing out one or two drops into a waste vessel and then drawing up the KCl by releasing the pressure. The capacity of the vessel and connections is quite small (1·5 c.c.), and there is no dead space so that if, for example, 5 c.c. of blood are drawn into the syringe and then used to fill the vessel, a good rinsing action is obtained and the last 1·5 c.c. cannot have lost any carbon dioxide. As an additional precaution the vessel may be filled with CO_2-free normal saline before introducing the blood. Saturated KCl is used in place of 3·5N here in order to conform more rigidly to the specifications for the standardisation of p_H measurements laid down by Clark (1928), although the difference will be very small for most buffer solutions. This apparatus permits the p_H determination to be made in the minimum time after withdrawing the blood from the blood-vessel, which is important in the study of the acid change in shed blood described by Havard and Kerridge (1929).
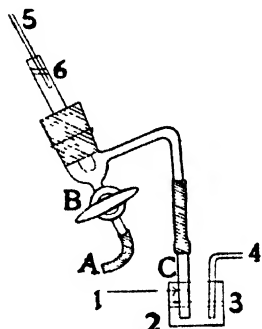
FIG. 8.—1 Junction.
2 Saturated KCl.
3 Liquid paraffin.
4 To 3·5 N KCl-Calomel cell.
5 To Phthalate - Calomel cell.
6 Liquid paraffin.

Glass Electrode Measurements in Viscous Solutions.

We have found that when glass electrodes of the MacInnes and Dole type are put into viscous solutions which are not strongly buffered, they do not immediately assume a potential characteristic of the solution, but that their potential rises or falls slowly to this value.   The phenomenon is indefinite, but is the more marked the greater the viscosity and the feebler the buffering power of the solution.   It was noticed first in protein and gum solutions, but we have reproduced it very satisfactorily in thousandth-molar phosphate solutions containing about 1000 grams of sucrose per litre.   The magnitude and direction of this drift depends on the p_H of the solution, on the p_H of the liquid with which the electrode has been washed, and apparently also on the p_H of the solution in which the electrode has previously been immersed for p_H measurement.   In view of the last-named factor, much time can be saved during a series of measurements with solutions of this type if they be done either in ascending or descending order of p_H values.   A large number of experiments have established conclusively that the drift is not due to change in the carbon dioxide content of the solution.   Thus, with a peptone-containing solution of p_H 8·9 the potential rose from 180 mv. immediately after the electrode—washed wth distilled water and dried with filter paper—had been inserted in the solution to a steady value of 201 mv. at the end of fifteen minutes.   The electrode was then removed, washed with distilled water, dried as before, and replaced in the solution.   The initial potential was 195 mv., and this rose again to 201 mv.   Electrodes differ widely in the extent to which they exhibit this phenomenon ; but we have not been able to correlate these differences with any differences in structure.   We have also observed the drift in Kerridge electrodes.   It was found that with MacInnes and Dole electrodes equilibrium was reached more rapidly if the electrode were moved to and fro in the solution, or, better still, if the pot containing the solution were mounted on a horizontal table rotated about a vertical axis by a small electric motor.   The liquid was then rotated for half-minute periods until the potential became constant.

Summary.

(1) Practical details are given for the construction and working of a simple thermionic valve electrometer which is capable of potential measurement with an accuracy of ± 0·05 mv. (equivalent to ± 0·001p_H) through a resistance of 10^9 ohms.

(2) Methods of testing the electrometer for errors produced by grid current and by various types of electrical leakage are discussed.   Necessary tests for electrical leakage round the membrane and for other possible faults in the glass electrode apparatus are also described.

(3) Convenient glass electrode systems are described, including one suitable for use with blood.   The use of MacInnes and Dole electrodes is advocated, and an improved method of mounting these electrodes is described.

(4) The special requirements for work of the highest accuracy are discussed.

(5) A sluggishness of the glass electrode has been observed in feebly buffered viscous solutions, and a method of minimising this is indicated.

also indebted to Mr. Watters of the Department of Physics of this hospital for valuable advice and for the loan of instruments.

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REFERENCES.

Biers, 1927, M.I.T. Thesis, cited by Scatchard and Buehrer, 1931, *J. Am. Chem. Soc.*, **53**, 574.
Clark, *J. Biol. Chem.*, **23**, 475, 1915.
Clark, The "Determination of Hydrogen Ions," 3rd edn., 1928. Baillière, Tindall and Cox.
Dole, *J. Am. Chem. Soc.*, **53**, 620, 1931.
Dubois, *J. Biol. Chem.*, **88**, 729, 1930.
Elder, *J. Am. Chem. Soc.*, **51**, 3266, 1929.
Elder and Wright, *Proc. Nat. Acad. Sci.*, **14**, 936, 1928.
Ellis, *J. Am. Chem. Soc.*, **38**, 737, 1916.
Fosbinder, *J. Physical Chem.*, **34**, 1299, 1930.
Guggenheim, *J. Am. Chem. Soc*, **52**, 1315, 1930.
Harrison, *J. Chem. Soc.*, 1528, 1930.
Havard and Kerridge, *Biochem J.*, **22**, 600, 1929.
Hughes, *J. Chem. Soc.*, 491, 1928.
Kerridge, *J. Sci. Inst.*, **3**, 404, 1926.
Livingston, Morgan and Campbell, *J. Am. Chem. Soc.*, **53**, 454, 1931.
MacInnes and Dole, *Ind. Eng. Chem.* (analytical ed.), **1**, 57, 1929.
MacInnes and Dole, *J. Gen. Physiol.*, **12**, 805, 1929a.
MacInnes and Dole, *J. Am. Chem Soc.*, **52**, 29, 1930.
Maclagan, *Biochem J.*, **23**, 309, 1929.
Mirsky and Anson, *J. Biol. Chem.*, **81**, 581, 1929.
Morton, *J. Sci. Inst.*, p. 187, 1930.
Müller, *Z. Electrochem.*, **36**, 923, 1930.
Partridge, *J. Am. Chem. Soc.*, **51**, 1, 1929.
Schwarzenbach, *Helv. Chim. Acta*, **13**, 865, 1930.
Stadie, *J. Biol. Chem.*, **83**, 477, 1929.
Unmack and Guggenheim, Det. Kgl. Danske Videns. Selsk., **10**, 8, 1930.
Voegtlin, de Eds and Kahler, *Am J. Physiol.*, **91**, 225, 1929.
Voegtlin, de Eds and Kahler, *United States Public Health Reports*, **45**, 2223, 1930.

PROTEIN STRUCTURE.

By Claude Rimington.

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Astbury and Woods'[1] fundamental work upon the crystalline structure of the protein of wool fibres and the hypothesis they put forward as an explanation of the changes observed in the X-ray pattern when such fibres are stretched, would seem to be full of significance for protein chemistry in general. Within the last ten years, different lines of evidence have been converging upon the view that some regularity, as regards pattern and molecular size, underlies the disordered confusion of data we possess relating to the proteins of the animal and vegetable kingdoms.

[1] Astbury and Woods, *Nature*, **126**, 913, 1930.

The classical theory of protein structure advanced by Fischer and Hoffmeister, and based upon the peptide linkage is felt to be insufficient in the light of modern experience. Alternative suggestions have not been wanting, but none of these has proved entirely satisfactory. Abderhalden's [2] hypothesis picturing the protein as made up of an aggregation of loosely-bound amino-acid anhydride (diketopiperazine) rings is not supported by unassailable evidence. Troensegaard's [3] theory ascribing to the amino-acids a secondary origin from the breaking up of complexes of pyrrole rings, ingenious though it is, fails to account for the fact that the amino acids recoverable from proteins after acid hydrolysis are optically active and not racemic mixtures. Similarly with other views. The great strength of the Fischer theory is that it alone accounts for the action of proteolytic enzymes ; the linkage it postulates, the simple peptide linkage, is the only one known to be attacked by these agents. Upon this as foundation, any complete and successful theory of protein structure must be built.

In its original form the Fischer theory depicts a protein as a gigantic peptide chain, slightly branched according to the possibilities offered by molecules like cystine and the dicarboxylic acids, but, nevertheless, a chain of almost incredible length having its terminal groups free. Individual differences between proteins and groups of proteins would then depend entirely upon differences in sequential arrangement of the constituent amino-acids of the chain. It is difficult to understand how such a structure could account for the known properties of proteins, both soluble and insoluble ; moreover, recent evidence [4] has shown that in the different classes of soluble proteins the molecule (micelle) is either spherical or nearly so. Again, the striking group resemblances (to be mentioned below), require a more rational hypothesis than this for their explanation.

That the amino and carboxyl groups of the amino acids are united by primary or secondary valencies in proteins appears to follow from the finding of Van Slyke and Birchard,[5] that the amount of nitrogen gas obtainable by allowing the protein to react with nitrous acid, corresponds almost exactly to the ϵ amino groups of lysine, as also from titration studies. Measurements of acid and base binding capacity have given results which should be interpreted with caution. In general, stoichiometric combination appears to take place, but adsorption phenomena may also intervene, see Sandstrom.[6] Bancroft's [7] recent work with his associates in which the vapour pressure of the systems solid protein $+$ HCl or NH_3 gas was followed, affords values for the equivalent weights of these proteins which are not in accord with those of any other observer ; the behaviour of some of the proteins is also different from that deduced from solution titration studies. It must be emphasised that the constitution of a protein may well be different in the solid and in the dissolved states, especially if the theory of reversibly-dissociable complexes be entertained.

Sørensen [8] has sought for criteria of purity whereby individual

[2] Abderhalden, *Naturwiss.*, **12**, 716, 1924; Abderhalden and Komm, *Z. physiol. Chem.*, **130**, 181, 1924.
[3] Troensegaard, *Z. physiol. Chem.*, **112**, 86, 1921.
[4] Svedberg, *Trans. Faraday Soc.*, **26**, 740, 1930.
[5] Van Slyke and Birchard, *J. biol. Chem.*, **16**, 539, 1913.
[6] Sandstrom, *J. physical Chem.*, **34**, 1071, 1930.
[7] Bancroft, *J. physical Chem.*, **34**, 449, 1930.
[8] Sorensen, *Koll. Z.*, **53**, 102, 170 and 306, 1930.

proteins could be characterised. Such a physical property as solubility at a given temperature and in presence of given salt and hydrogen ion concentrations should serve ; it was found, however, that under these conditions the quantity of egg albumin dissolved increased as the total amount of protein in the system was increased. Moreover, in the case of crystalline serum albumin it was not possible to prepare samples exhibiting the same solubility, even under identical conditions.

These findings led Sørensen to the suggestion that proteins, even after repeated crystallisation, are not to be considered as single entities but as reversibly dissociable systems of complexes, a view which he has since vindicated experimentally by a series of researches upon the fractionation of proteins such as egg and serum albumins, serum globulin, gliadin and casein. Fractions were obtained having differing solubilities and chemical composition, which by reunion regenerated a system indistinguishable from the original protein.

Sørensen was not able to account for the wide differences in solubility of these fractions, since acid and base binding measurements gave identical figures, as did also measurements of osmotic pressure.

As a result of this work, it is necessary to conclude that familiar biological fluids, such as blood, containing proteins, actually comprise a system of complexes in equilibrium, and that when this equilibrium is disturbed by " salting out " or otherwise, a process of association goes on leading to the deposition of a less soluble system and attainment of a fresh equilibrium. Albumin and globulin, therefore, lose their individuality.

Such dissociated complexes as these need not, however, possess the same chemical composition ; in fact, experiments shows that they do not. In this way it is permissible to think of two (or more) types of complex, which are fundamentally different from one another and pass habitually, in the presence of high concentrations of salts, into the albumin or globulin type of system respectively.

There are, undeniably, certain marked resemblances between members of any one class of proteins which it would be difficult to imagine were fortuitous. Thus, serum albumin can be crystallised with ease, as can also the dissociated fractions obtainable from it, whereas the serum globulins can under no circumstances be induced to crystallise. Again, the limits of concentration at which " salting out " commences are similar with a variety of salts for different members of a group.

More recently, Svedberg [9] has devised a means of ascertaining the molecular or micelle size of proteins in solution, using an ultra-centrifuge and measuring either the sedimentation velocity or sedimentation equilibrium, the former affording also data as to the homogeneity of the dispersions, the symmetry of the particles, and so on. His results are particularly striking, and are a challenge to the chemical theory of protein structure. Briefly, it was found that a number of the proteins examined were mono-disperse and that the molecular weights or particle weights of these, fell without exception into four groups having weights of one, two, three and six times 34,500. Moreover, reversible dissociation into particles of the common size was observed in the second, third and fourth groups.*

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[9] Svedberg, *Koll. Z.*, **51**, 10, 1930.
* A separate additional class was distinguished, the members of which all had particle weights of the order of millions.

Such a finding can only mean that there is some structural organisa-tion common to all protein systems.   In some cases, Svedberg [10] noted that a certain minimum concentration of protein was necessary before homogeneity in particle size was obtained, an observation which recalls Sørensen's demonstration that dissociation, in systems such as gliadin, occurs only when the total protein concentration is very low.   Perhaps 34,500 does not represent the lowest size of dissociable complex, but the dominance of this figure throughout all the groups nevertheless requires an explanation.

Should there be some structural pattern common to all proteins, this should be demonstrable both chemically and physically.   In the former sense, the efforts of various workers have met with little success, most probably because the methods of experimental attack have not been sufficiently refined, but the success of the X-ray diffraction method in elucidating the structure of cellulose and other polysaccharides leads to the hope that in the region of protein chemistry also this weapon may prove of service.

Early investigators of crystallised protein preparations were in some instances unable to observe structural regularities by the X-ray method, and hence were led to the conclusion that such substances did not form crystals in the true sense of the word; Herzog and Jahncke [11] failing to get positive results with hæmoglobin and serum globulin, proposed to designate such forms " pseudo-crystals." It has been pointed out by Ott, [12] however, that in examining protein preparations by this means, errors are likely to be introduced, which are not present, or are at any rate, less evident in experiments made with other organic substances giving much more powerful reflections. Using a pure specimen of egg albumin (prepared in the crystalline state by Sørensen) suspended in ammonium sulphate solution within a collodion sack, and the rays from a copper kathode, Ott was able to observe well-marked diffrac-tion rings due to the protein, with angles of 8° 45', 14° 15', and 21° 10', so proving that in this case at any rate, the material was truly crystalline. Silk fibroin, [13] has been fairly extensively studied, since it yields a well-defined diffraction photograph and the material is easily mounted for examination ; within the past few months Astbury and his co-workers have succeeded in postulating a structure for wool keratin, which meets the main requirements of their X-ray analyses quantitatively and also accounts satisfactorily for some of the physical properties, such as elastic deformation, of the wool fibre. In particular, Astbury finds that in an atmosphere of steam the fibre is capable of nearly 100 per cent. extension, whilst simultaneously the X-ray pattern undergoes a pronounced alteration. The protein in the fully-extended state, designated " β keratin " is assumed to consist of a series of peptide chains lying with their length roughly parallel to the axis of the fibre (a constitution similar to that proposed by Meyer and Mark for silk fibroin), whilst in the normal, unextended state this chain becomes bent back upon itself, deformed in such a way that adjacent peptide groups become contiguous. According to this scheme, anhydride formation with the production of true diketopiperazine rings does not take place,

[10] Svedberg and Sjögren, *J. Amer. Chem. Soc.*, **50**, 3318, 1928.
[11] Herzog and Jahncke, *Naturwiss*, **9**, 320, 1921.
[12] Ott, *Kolloidchem. Beih.*, **23**, 108, 1926.
[13] Meyer and Mark, *Ber.*, **61**, 1932, 1928.
[14] Herzog and Jahncke, *Fest. Kaiser-Wilhelm-Ges.* 118, 1921.

but the secondary valencies of the $>$ CO and $>$ NH groups are sufficient to give the system stability and hold the loops of the chain in their respective positions (see Fig. I.)

Whilst, of course, further evidence will be necessary before this concept can be finally established, there is much in the view which has far-reaching significance. Thus, it is noticeable that this alteration of the peptide chain by tension has been achieved in a fibre where orientation is already established. We must not lightly reject the possibility, however, that in similar circumstances it could occur with other proteins, a point which might be tested by using N. K. Adam's method of compressing orientated surface films. The poineer work of Gorter and Grendel [15] in this field indicates that valuable results may be yielded in time by a systematic application of the method. May it not be that we have to look for an explanation of the phenomenon of protein denaturation in the direction of this hypothesis?

Denaturation has, until recently, been regarded as an irreversible change, but Anson and Mirsky [16] have shown that under suitable conditions denatured globin may be redispersed in the undenaturated form. Internal structural changes, such as those involving the sulphur groups, are known to attend denaturation. There is, however, no scission ; the osmotic pressure [17] and the number of titratable acidic and basic groups remains unchanged.[18] The loss of iso-electric solubility must be the result of change in some internal tautomeric configuration.

Making the assumption that denatured proteins possess the contracted " α keratin " type of peptide chain, it is understandable that the tendency to dissolve in aqueous systems becomes lost owing to those groups possessing positive polarity, the CO-NH groups becoming transformed into virtually closed ring systems. Neither acid nor base binding nor particle mass would be altered by such a change.

As a working hypothesis it might be suggested, tentatively, that the elementary complex of protein systems in general consists of a number of peptide chains containing the amino-acids characteristic of the protein, these chains being grouped together and held by co-valence forces in micelles of the order of $2 \cdot 2 \mu\mu$ radius corresponding to a molecular weight of 34,500. Such micelles would comprise the units comparable with the crystallites of cellulose, and would possess a weaker power of association, varying chiefly with the hydrogen ion concentration, than do the individual members of the micelle.

In fibres such as wool and silk, physical forces have resulted in an orderly arrangement of the micellar units, with resulting clarity of X-ray pattern ; in the majority of soluble proteins, however, in the absence of an orientating field, it is natural to conclude that the arrangement is haphazard, and this makes the experimental examination of such systems by the diffraction method a difficult task. It may be suggested, however, that in common with what we know of the structure of other surface films, a natural orientating force may be sought for and found in the phenomena which take place at the phase interface. The peculiar rigidity acquired by the surface of an aqueous egg albumin solution when at rest and the instantaneous disappearance of the former

[15] Gorter and Grendel, *Biochem. Z.*, **201**, 391, 1928 ; also *Proc. Acad. Sci. Amsterdam*, **32**, 770, 1929.
[16] Anson and Mirsky, *J. gen. Physiol.*, **4**, 469, 1930.
[17] Huang and Wu, *Chinese J. Physiol.*, **4**, 221, 1930.
[18] Booth, *Biochem. J.*, **24**, 158, 1930.

5·15 Å.

10·2 Å.
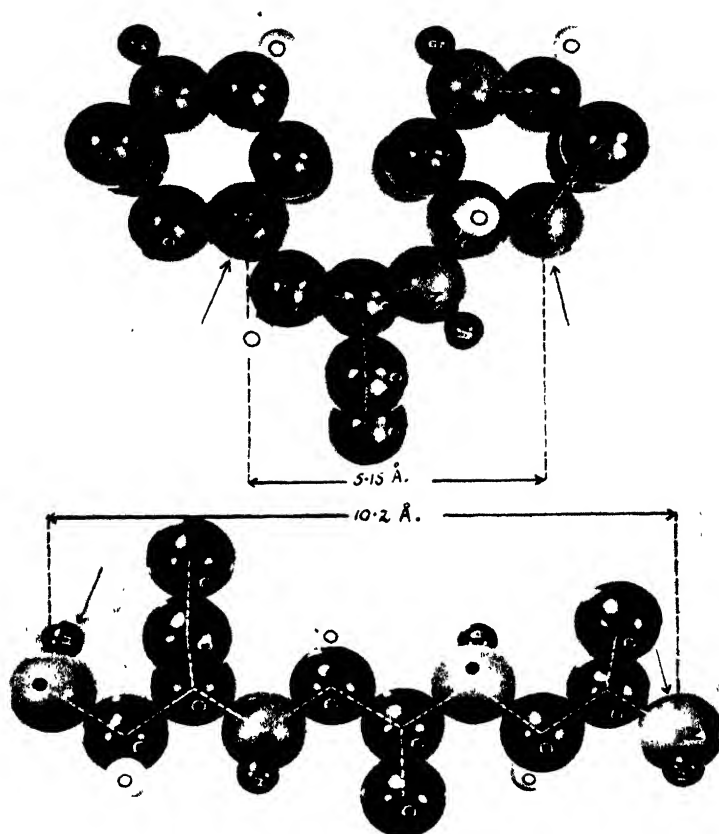
FIG. 1.   [To face p. 226.

when the liquid is agitated, is a well-known phenomenon suggesting that the possibility of experimental examination under these conditions is worth looking into.

Gorter and Grendel [15] have recently shown that when proteins are allowed to spread upon the surface of tenth-normal hydrochloric acid, the *same* area per milligram is occupied by all, whether they belong to the class with micelle mass (Svedberg) of 34,500 (= A) or those of two, three or six times this figure. The micelles lie flat along the surface of the liquid. In other words, these workers have shown that the forces bringing about surface orientation and spreading are sufficient to overcome intermicellar cohesion and produce *complete* (but reversible) dissociation of the 6A protein into micellar units of the common size A (34,500).

Orientation of a somewhat similar character brought about by an applied mechanical force is described by Muralt and Edsal [19] in their study of the double refraction of flow of muscle globulin preparations. The solution was placed between two concentric cylinders, the outer one being kept in rapid rotation. Although the theory of double refraction of flow is imperfectly developed, Muralt and Edsal were able to come to the conclusion that the micelles or molecules of their protein preparation were mono-disperse, in marked contrast to V_2O_5 sols, which have also been studied extensively under these conditions.

Discussing Svedberg's ultracentrifuge experiments, King [20] has pointed out that the data fail to show whether reversible dissociation, at p_H values removed from the iso-electric point, actually takes place independently of the applied gravitational force and has asked whether steric hindrance may not be overcome and hydrolytic action promoted by similar means.

Modern views upon enzyme action have accustomed us to the idea of electronic deformation or " activation " of the substrate molecule when closely adsorbed upon the catalytic agent ; taken in conjunction with what has been said above, it is not improbable that actual mechanical deformation may occur, in addition, at the enzyme surface as a result of the relatively large forces involved, spatial distortion thus playing a part, possibly an essential part, in overcoming the cohesive forces of a normally stable molecule. A good example of alteration in internal configuration as a result of catalytic activity is to be found in the case of the isomerisation of cymarin to allocymarin recently studied by Jacobs. [21]

Attempts to apply X-ray analysis directly to animal muscle fibres have not resulted in great success. A period of identity of about 10 Å.U. was observed by Herzog and Jahncke, [22] but no trustworthy inference is as yet possible from these measurements. The theory of the micellar structure of proteins needs to be more fully developed from the structural chemical point of view before any fruitful attempt can be made upon the analysis of physiological systems ; in particular, suitable technique awaits development whereby information may be gained concerning the internal structural changes which may take place within the micelle groups of simple protein preparations when artificial orientating forces are applied to them.

[19] Muralt and Edsal, *Trans. Faraday Soc.*, 26, 837, 1930.
[20] King, *Trans. Faraday Soc.*, 26, 747, 1930.
[21] Jacobs, *J. biol. Chem.*, 88, 519, 1930.
[22] Herzog and Jahncke, *Ber.*, 53, 2162, 1920.

Note Added in Proof.—Since this article was sent to press, a further communication has appeared from Astbury and Woods [23] in which an attempt is made to explain the significance of the figure 34,500 encountered in connection with Svedberg's ultracentrifuge experiments. It is suggested that the length of a peptide chain is limited simply by vibrational instability.

Although no quantitative calculations are presented in support of the suggestion, it is nevertheless shown that a chain length corresponding to a molecular weight of 33,500 is in harmony with the X-ray and elastic data obtained upon wool and hair. In particular, the phenomenon of decay of tension in moist, stretched hair, is interpreted in terms of chain stability.

Proceeding from the view that the protein is comprised of chains of amino-acids in peptide linkage, Astbury and Woods also show that the existence of Svedberg's molecular weight groups of 1, 2, 3, and 6 times the common factor follows naturally as a result of the possible ways of combining such peptide chains in a crystallographic unit. The 6 × 34,500 structure, for example, is a threefold screw of pairs of chains pointing in opposite directions, and is thus analogous in pattern to a crystal of quartz.

Whilst these suggestions undoubtedly provide the first rational explanation of the phenomena observed in the ultra-centrifuge, it is nevertheless difficult to see how the living cell is able to achieve such precision in its work of synthesis and intramolecular arrangement when so much, even in the finished system, appears to depend upon chance and the law of averages. The problem of biological specificity becomes even more intricate than ever!

DECOMPOSITION OF ALKALI CHLORIDES AT HIGH TEMPERATURES.

By F. C. Guthrie and J. T. Nance.

During the preparation of pure sodium chloride for experiments on the heat of solution of salt coloured by cathode rays,[1] it was observed that fusion in a platinum dish always produced a specimen which was slightly alkaline. The statements in the literature on this point are somewhat conflicting, but most of them indicate that sodium chloride is not decomposed by fusion in air.

In his Treatise on Inorganic and Theoretical Chemistry, Vol. II., page 553, Mellor states that "sodium and potassium chlorides are not altered in composition by fusion in air, but lithium chloride becomes alkaline and loses chlorine. According to H. Schulze, if sodium chloride be heated to redness in the presence of oxygen, a trace of chlorine is produced."

Richard and Wells [2] on page 514 state that "It appeared from tests with indicators that the salt (NaCl) remained strictly neutral after fusion in a vacuum as it did in the air." Other authors state that sodium chloride vapour is dissociated by steam.[3]

If sodium chloride be fused in a platinum dish or crucible by means of a blowpipe it undoubtedly becomes alkaline on subsequent solution in water. In one experiment, in which 11·6 grams of sodium chloride were fused in a platinum dish for five minutes, the alkali found in the

[23] Astbury and Woods, *Nature*, 127, 663, 1931.
[1] *Nature*, 123, 130, 1929.   [2] *J. Amer. Chem. Soc.*, 27, 459, 1905.
[3] *Ber.*, 40, 1482, 1907 ; and *J.C.S. Proc.*, 162, 1914.

subsequent solution required 8·1 c.c. of N/100 HCl. Even potassium chloride treated in the same way gave a slightly alkaline solution.

An extensive series of experiments has been carried out on the decomposition of alkali chlorides at temperatures up to 1000° C., in several different gases, under varying conditions of gas stream velocity and duration of heating. The decomposition effected was determined by titration of the alkali produced, by means of standard acid. Under certain conditions with lithium chloride about 7 per cent. decomposition was obtained, but volatility of the alkali chloride and of the products of decomposition prevented absolute determinations being made. It was not possible to collect the volatile products of decomposition because no available material could be found for the construction of an electric tube furnace, which would resist the attack of alkali chloride vapour and at the same time be non-porous. Silica and fire-clay were rapidly attacked with evolution of chlorine, and in the case of the former substance a thick muffle wall was attacked throughout. Alundum appears to be resistant to alkali chloride vapour, but it is too porous to retain gaseous products.

In view of this difficulty most of the experiments were carried out by heating the chlorides in a platinum crucible, fitted with a lid and small platinum tube for introduction of the gas used. The assembled crucible was suspended by this tube in an electric muffle furnace, the temperature of which was measured by means of a platinum and platinum rhodium couple.

Most of the experiments in which the effect of different gases and of the variation of temperature were investigated, were carried out on lithium chloride, as this salt naturally gave a maximum decomposition. The marked difference in the behaviour of the alkali chlorides with increase in atomic weight is shown by the results given in Table I. In each of these experiments the temperature was approximately 820° C., the duration of heating was thirty minutes and the gas stream used was a rapid current of air of about 1400 c.c. per minute calculated at room temperature.

TABLE I.

Chloride used.	Weight of Chloride left after Heating.	c.c. of N/10 HCl for Titration.	Percentage Decomposition.
LiCl	2·61	6·5	1·0
NaCl	2·95	0·3	0·06
KCl	2·17	0·1	0·03
CsCl	1·51	nil	nil

The cæsium, potassium and sodium chlorides were purified to remove salts of alkali metals of lower atomic weight.

The experiments on lithium chloride were carried out to determine the effect of varying the following factors on the amount of alkali found in the residual salt : (1) Temperature ; (2) Duration of heating ; (3) Amount of salt remaining at the end of the experiment ; (4) Rate of gas stream through the crucible ; (5) Nature of the gas used.

1. Temperature.

Lithium chloride was not decomposed when heated in a slow current of moist air, provided the salt was not melted. At temperatures above

the melting-point slight decomposition was observed, and the effect increased with temperature.

Using a current of moist air of approximately 100 c.c. per minute the results shown in Table II. were obtained.

TABLE II.

Temperature.	Duration of Heating in Minutes.	Weight of LiCl left after Heating.	c.c. of $N/10$ HCl for Titration.	Percentage Decomposition.
594° C.	124	2·45g.	nil	nil
625	123	2·62	0·65	0·1
854	120	2·11	2·8	0·5
1000	120	1·75	4·18	1·0

Although lithium chloride is quite stable just below the melting-point in air, slight decomposition was observed at about 75° C. below the melting-point when a rapid current of nitrogen, saturated with water vapour at 75° C., was passed through the crucible, as indicated in Table III.

TABLE III.

Temperature.	Duration of Heating in Minutes.	Weight of LiCl left after Heating.	c.c. of $N/10$ HCl for Titration.	Percentage Decomposition.
532° C.	30	2·06 g.	0·3	0·06
575	30	2·03	1·1	0·23
606	30	1·99	8·8	1·9

The speed at which the saturated nitrogen was passed was approximately 1400 c.c. per minute.

Using a rapid stream of superheated steam decomposition was observed even at 170° below the melting-point, and a more marked increase occurred at temperatures over the melting-point than in the previous series of experiments (see Table IV.).

TABLE IV.

Temperature.	Duration of Heating in Minutes.	Weight of LiCl left after Heating.	c.c. of $N/10$ HCl for Titration.	Percentage Decomposition.
430° C.	30	2·0g.	0·1	0·02
530	30	2·0	0·75	0·16
590	30	2·0	1·25	0·26
650	28	2·0	26·4	5·6
730	30	2·0	47·0	10·0

The speed at which superheated steam was passed through the crucible was approximately 1·47 grams per minute. Using the same weight of steam in each of the above experiments, of course involves a greater velocity at the higher temperatures. Later experiments show that a small part of the increased decomposition in the above series is due to this factor, which, however, it was not practicable to eliminate.

2. Duration of Heating.

The amount of alkali formed increases with the duration of heating as indicated by the experiments recorded in Table V.

TABLE V.

Temperature.	Duration of Heating in Minutes.	Weight of LiCl left after Heating.	c.c. of $N/10$ HCl for Titration.	Percentage Decomposition.
650° C.	28	2·0g.	26·4	5·6
650	90	1·9	51·3	11·5
660	250	2·1	77·2	16·3

Superheated steam at approximately the same speed was used in each case. The alkali produced appears to be nearly proportional to the square root of the time of heating.

$$\frac{26\cdot4}{\sqrt{28}} = 4\cdot99, \quad \frac{51\cdot3}{\sqrt{90}} = 5\cdot41, \quad \frac{77\cdot2}{\sqrt{250}} = 4\cdot88.$$

This relationship was observed by Vanzetti and Oliverio [4] in a somewhat analogous case.

3. The Amount of Salt Remaining at the End of the Experiment

Other things remaining constant, the greater the amount of salt remaining at the end of the experiment, the greater the amount of alkali produced, though the percentage decomposition was less. In most of the previous experiments the initial weight of salt was less than 2·5 grams, the aim being to leave 2 grams at the end of the experiment. In the following series (Table VI.) the initial weight was varied widely.

TABLE VI.

Temperature.	Duration of Heating in Minutes.	Weight of LiCl left after Heating.	c.c. of $N/10$ HCl for Titration.	Percentage Decomposition.
895° C.	120	0·66g.	1·65	1·03
900	120	2·62	3·95	0·64
895	120	6·5	7·6	0·49

A slow current of moist air was used in these experiments, and this accounts for the small extent of the decomposition.

4. Rate of Gas Stream through the Crucible.

This factor makes a considerable difference at a high velocity but has no appreciable effect below 400 c.c. per minute, when an approximately constant minimum effect is obtained. This is indicated by the series of experiments (Table VII.) in which moist air was passed at varying speeds.

[4] *Gazzetta*, **59**, 288, 1929.

TABLE VII.

Tempera- ture.	Duration of Heating.	Final Weight of LiCl.	Air Current c.c./minute.	c.c. of $N/10$ HCl for Titration.	Percentage Decomposition.
780° C.	227 min.	2·03g.	nil	4·55	0·95
780	221	2·01	21	3·75	0·8
770	225	2·1	81	4·8	0·97
785	215	2·06	386	4·85	1·0
775	173	1·76	1390	8·0	1·93
780	220	2·38	7300	17·25	3·1

In these experiments the air stream velocity is calculated at the temperature of the experiment. The minimum effect indicates that there must be some purely thermal decomposition, and this is supported by three experiments which were carried out, using air or oxygen which had been intensively dried by passage over three long columns of phosphorus pentoxide. In the first of these experiments, with lithium chloride at the same temperature as in the last series, approximately the same minimum decomposition was obtained, and in the third experiment even sodium chloride showed some decomposition (Table VIII.).

TABLE VIII.

Tempera- ture.	Duration of Heating.	Final Weight of Salt.	Intensively Dried Gas c.c./minute.	c.c. of $N/10$ HCl for Titration.	Percentage Decomposition.
780° C.	230 min.	2·2g. LiCl	Air 21	4·3	0·83
955	223	1·71 LiCl	,, 21	5·05	1·26
890	330	8·75 NaCl	Oxygen 113	0·3	0·02

5. Nature of the Gas used.

Using either moist air or moist nitrogen about the same results were obtained, but with moist hydrogen a slightly greater amount of alkali was produced. In the case of carbon dioxide considerably more decomposition occurred and lithium carbonate was found in the remaining lithium chloride. Using nitrogen saturated with water vapour at 75° C., and in the case of superheated steam, much more of the chloride was decomposed. In the following series of experiments (Table IX.), the full effect of superheated steam is not shown because the experiment in which it was used, was carried out at a lower temperature.

TABLE IX.

Temperature.	Final Weight of LiCl.	Gas used.	c.c. of $N/10$ HCl for Titration.	Percentage Decomposition.
810° C.	2·51g.	Moist nitrogen .	8·0	1·36
810	2·61	,, air . .	6·55	1·07
810	2·8	,, hydrogen .	9·55	1·45
810	2·54	,, carbon dioxide .	18·3	3·05
810	2·43	Nitrogen sat. at 75° C.	35·4	6·2
730	2·02	Superheated steam .	47·0	10·0

In these experiments the duration of heating was thirty minutes in each case, and the gas current was at the rate of about 5000 c.c. per minute calculated at the temperature of the experiment.

Summary.

Part of the object of this research was to ascertain under what conditions the alkali chlorides could be completely dried without decomposition. The experiments carried out indicate that these chlorides, including lithium chloride, may be heated at temperatures below the melting-point, in a slow current even of moist air without decomposition taking place, but that it is inadvisable to melt them.

At higher temperatures the most important factor in the decomposition of these chlorides is the concentration of water vapour in the gas passed over the liquid surface. There must, however, be some purely thermal decomposition above the melting-point, in view of the fact that in experiments in which a slow stream of very dry air was used, almost as much decomposition of lithium chloride was observed as in parallel experiments using moist air.

The volatility of the chlorides and products of decomposition, and their corrosive action on available refractories made it impracticable to carry out such quantitative experiments as would be required for the complete elucidation of the nature of the reactions.

The authors are indebted to Professor E. C. C. Baly, F.R.S., for the facilities for carrying out this research.

REVIEWS OF BOOKS.

The Physical Properties of the Soil. By BERNARD A. KEEN. London :
    Longmans, Green & Co. Ltd. Pp. vi + 380 (bibliography 18 pages).
    93 diagrams and 2 plates. 21s. net.

This scholarly book is an important addition to the Rothamsted Monographs in Agricultural Science of which series it forms the fifth member.

The book opens with an historical introduction of 36 pages in which is traced the evolution of agricultural implements as the outcome of increasing knowledge of the physical properties of the soil. This is the principle underlying the book, which treats, as the main business of soil physics, the analysis of those properties on which cultivation is based. Accordingly attention is directed to particle size, flocculation and dispersion, plasticity, and water movement, as of special importance in agricultural practice. No attempt is made to avoid rigorous treatment, and whilst it is feared that few agricultural students will tackle the mathematical development of the theory say, of sedimentation or plastic flow, it is well that all concerned should have their attention drawn to the bearing it has on agricultural science ; much good will result if it leads to an improvement in the physical and mathematical equipment of the student (to say nothing of the instructor).

After the introduction, the main portion of the book is devoted, as is fitting, to the discussion of soil-water relationships, the succeeding chapters dealing with mechanical analysis and the properties of soil-water systems varying in composition from field moisture content to thin suspensions. The remaining chapters are concerned with cultivation, soil temperature, and gaseous movement.

It is perhaps no more than natural that prominence should be given to Rothamsted investigations : this seems to have led to some lack of perspective in the allocation of space. Thus whilst very full descriptions are given of the

Oden-Keen balance for sedimentation analysis and the soil dynamometer, and the (often published) official method for Mechanical Analysis, little help is given to those desirous of making such measurements as permeability, the Atterberg number, moisture equivalent, and heat of wetting, all of which have become important for both routine and research purposes. That a full description (pp. 82-88) of the Oden-Keen balance was considered necessary is surprising, as it is stated (p. 68) that its use involves errors inherent in the technique which cannot be corrected.

Where chemical matters enter, there is room for some criticism. The American workers do not use the ratio of silica to alumina for the characterisation of clay, but silica to sesquioxides (p. 191). Chemical formulæ are used frequently where it would have been better to name fully the compounds especially minerals, *e.g.* p. 148. (Why are chemical formulæ so dear to the non-chemist?) The "loss on ignition" of the mineral portion of a soil cannot possibly be a measure of the inorganic colloid of a soil, owing to the great variation in combined water content of different soil colloids ; thus that from the very "colloidal" material bentonite, occurring in the gumbo soils of America, loses on ignition only about one-half or one-third of that of a non-plastic lateritic clay.

Doubtless such matters can be adjusted in a future edition : meanwhile it is to be hoped that all students and research workers will give it the careful attention it deserves, which will be to their great profit.

Theoretical Physics. By W. WILSON, F.R.S. Hildred Carlile Professor of Physics at Bedford College, London. Vol. 1. Mechanics and Heat : Newton-Carnot. 22 × 14 cm. (London : Methuen & Co. Pp. x + 332. 80 diagrams. Price 21s.)

The declared purpose of this work is "to present an account of the theoretical side of physics which, without being too elaborate or voluminous, will nevertheless be sufficiently comprehensive to be useful to teachers and students."

This is an ambitious aim and is somewhat contrary to the present tendency ; the days of encyclopædias are past. Nevertheless it is a salutary endeavour to make. Monographs on individual parts of a subject are exceedingly useful at the present time when the spirit of change is in the air, but they are apt to give an impression of isolation. No part of science can exist on its own revenues alone. For this reason we welcome Professor Wilson's attempt to produce a co-ordinated treatise in which a general survey will be made "from the point of view of exhibiting the unity of physical theory." The present is the first of the three volumes in which it will appear.

This volume is devoted to Newtonian physics—using this term to include all developments which were interpreted strictly in accordance with Newton's laws of motion. A door is kept open throughout enabling an escape to be made in the later volumes into the more ætherial regions of Relativity and Quantum Theory. In fact Newtonian theory is regarded as antecedent to and anticipatory of the wider theories which appear to be necessary if the unification of physical knowledge is to be perfected. It may be expected that the later volumes will be more speculative than the present one and rest on more incomplete (if not, more insecure) observational basis. The present deals with the detailed facts which accumulated from Newton's time up to the end of the nineteenth century. To label it from Newton to Carnot (the latter of whom died in 1832) is somewhat open to criticism, since it appears to imply the omission of the law of the conservation of energy (including heat changes) which was not acknowledged as a

recognised principle of physics until 1850. Needless to say the application of this principle is fully treated in this book.

The first 270 pages are devoted to the subject often known as the mixed mathematics, including a pure mathematical introduction outlining the tensor calculus which is used throughout. If it had been called the mathematical theory of physics its character would have been adequately indicated. This statement introduces a very vexed question. An old-fashioned physicist who was taught to regard (and still does regard) experiment and observation as being the foundation of physics and who merely called in mathematics as a handmaiden whose work consists in putting things in order—arranging them so that they can easily be found by the aid of symbols—must join with Sir Arthur Schuster in regarding "with the gravest concern a growing school of scientific thought which rests content with equations correctly representing numerical relationships between different phenomena even though no precise meaning can be attached to the symbols used."

The isolation of the mathematical from the experimental and the rest of the theoretical parts of physics, we believe not to be good training for a student, and we hope that this book will be studied along with experimental work and critical instruction in the theory of such work. As an aid to understanding we have little but praise to say about it, though it may be found rather hard except by post-graduation students. Unfortunately mathematical treatment often ends just where the phenomenon begins to be thoroughly interesting. For example, in spite of the display of symbols, elasticity is limited to infinitesimal strains—in practice the chief interest arises in connection with large strains. Unless, we have overlooked it there is no hint given of this. If the foundations of the world are indeed laid in mathematics, surely a new kind has yet to be discovered in order that we may deal with the breaking of a stick as easily as it occurs in nature. Or perhaps, after all, the apparent mathematical character of the universe is merely an illusion which has been gradually generated by our habit of enumerating our possessions on our ten fingers.

The final chapter (pp. 272-325) on thermodynamics is rather crowded out by the other matter and can only be regarded as an outline. We regret the attempt to restrict the term "adiabatic" to reversible changes : partly because this is contrary to universal custom (in practice it means *no thoroughfare* for heat, without restriction) and partly because, at once a new name will be required for such changes in irreversible processes. If there is a name which requires altering it is "isothermal" which might equally well stand for an adiabatic ; the better name would be *isothermometric* for changes in which the temperature remains constant.

We prefer Clausius' treatment of the second law to that of Planck (p. 288). With regard to Kelvin's *first* absolute scale of temperature it might be added that he put it forward before the law of efficiency was known. It must be pointed out in connection with the phase rule (p. 321) that it is necessary carefully to define what is meant by a *constituent;* because a particular technical meaning *must* be given to it in order that the phase rule should be true. For this reason it is usually distinguished by being called a *component* and its meaning is then carefully stated. There is no point on which a beginner is more liable to go wrong.

We may add, what has probably been surmised, that the book is suited to higher classes in physics in a university. Both student and teacher will learn much from it. We hope, however, that the teacher will link it up as much as possible with the less mathematical side of the subject.

Les Applications des Rayons X. By J. J. TRILLAT. (Paris : Les Presses
  Universitaires de France. Pp. 298, with 16 plates and 108 figures.
  Price 85 francs.)

The rapidity with which the X-ray technique has been applied to the
measurement of molecular orientation in liquids and solid substances is very
remarkable. Not only has its value been proved in the determination of
crystal structure, but it has also met with very considerable success in fields
which are of vital importance in industry. In metallography, it has been
employed in the investigation of the changes in particle size occurring as a
result of deformation and thermal treatment, and in this field it has found
a notable application in the study of the optimum size of grain of catalytic
substances. The method has also found a wide range of usefulness in the
examination of bodies which were formerly left to the colloidal chemist, for
example, cellulose, indiarubber, gelatine, resins, etc. The application of
the X-ray technique to the study of the changes which such substances
undergo in processes of manufacture has placed many industries on a
scientific basis.

The monograph which has now been published by M. Trillat is concerned
mainly but not entirely with the industrial application of X-ray methods.
In addition to the description of these applications, the author has surveyed
the information that is available on long chain organic compounds, on the
structure of colloidal particles, on the liquid and mesomorphic states, and
on the utility of the X-ray method in qualitative and quantitative chemical
analysis.

As an introduction to the industrial section, the author devotes 100 pages
to a description of the methods of production of X-rays and the spectro-
graphic methods employed. The survey of the methods is very exhaustive,
and copiously illustrated by diagrams. It is not his intention to supply the
details of the theoretical treatment of X-ray methods but to refer the reader
to special treatises for such information. The author, however, gives an
introductory survey of the generalities of X-rays, which is sufficient for an
understanding of what is written subsequently. The first part of the book
will prove very valuable to workers in this field, not only on account of the
methods described but also on account of the very full bibliography supplied
at the end of each chapter.

There is no index, which is a serious disadvantage in a work of this kind.
There is, however, a table of contents embodying the subject matter of each
chapter, which serves as a substitute for an index.

<div align="right">W. E. G.</div>

Flow and Measurement of Air and Gases. By ALEC. B. EASON, M.A.
  With illustrations. Second Edition. 15 cms. × 22 cms. (London :
  C. Griffin & Co., Ltd. Pp. xii + 254. Price 20s.)

In an official department there must needs be a great accumulation of
records which concern the work of the particular department and which often
lie buried there.

The present book appears to be the contents of a *dossier* on the flow and
measurement of air and gases, in pipes, in pneumatic tube problems, in air
compressors, measurement by means of hot-wire anemometers and subsidiary
questions relating thereto.

The drawback of the volume seems to be the plethora of the information
provided and the scantiness of the explanatory matter. Thus, the coefficient of

friction ζ is nowhere very clearly defined, at any rate not in such a way that a new-comer can see at once what its meaning is.   On page 25 we are told that it is independent of the system of units used and next that it "represents the proportionate loss of velocity head in a length of pipe"; and also, in connection with Table 2·2, that it is independent of the diameter and in Table 2·3 it is given as depending on the diameter.   The quantity named ζ at first reading appears to be of a protean character; later on it becomes clear that all that is meant is that, at first, it was thought sufficient to take it as an absolute constant, but afterwards it was recognised that its value (while still remaining a mere number) is different for tubes of different diameters.

In Table 2·4 are given thirteen different values of the quantity called ζ intended for use with the formulæ of the authors whose names are given; and these are followed by twenty-four more of later date.   No attempt is made to correlate these.   These lists are followed by a section "discussing" various authors' formulæ; most of the authors are additional to those already quoted, and the discussion amounts at most to a statement of the range for which each author claims his formula to be valid, but sometimes not even that amount of elucidation is provided.   In many cases the cited author merely quotes some one else, thus Carpenter quotes Arson, Hausbrand quotes Schmidt, Barker quotes Rietschel, and so the information is handed on without any guide as to its real value.

Now to serve up all this shows great impartiality, but the first impression on a reader is one of absolute bewilderment.   Much of the information is known to be worthless, having been obtained under imperfectly specified conditions of experiment.   What the reader wants is a guide through this welter of waste material so that he can distinguish the valuables that are certainly there.

The author himself seems to recognise this.   On page 65e (at the end of the chapter) he says : "When one sees tables 2·2, 2·3, 2 4 it seems rather hopeless to come to any conclusions," and he proceeds to give approximate values of ζ to be used in particular cases.   This section (together with the charts) is the most valuable part of the chapter; it appears to have been added in this, the second, edition.   The reader may find it and be content.   We think, however, that much might have been omitted and more elucidation added in the fifty-five pages of this chapter.   It is all the more necessary that a worker should be clear concerning the matter of this chapter inasmuch as it is fundamental to the substance of all the rest of the book.

The chapter on electric velocity meters is probably the best in the volume; that on flow from orifices is also treated in a scientific way.

One good feature is that at the end of each chapter a list of all the symbols used in the chapter is given on a folded sheet which when unfolded enables the list to be visible at the same time as the text.

The name of Poiseuille (the father of the flow in fluids) is badly mangled throughout—the left i being misplaced and the right-hand one removed.   No wonder that at the same time an extra sibilant appears.

The Spirit of Chemistry.   By Professor ALEXANDER FINDLAY.   (London : Longmans, Green & Co., Ltd., 1930.   Pp. xvi and 480.)

This volume is intended particularly for those whose desire it is to know something of chemistry as part of a generous education.

The author of "Chemistry in the Service of Man" has with nicety combined a historical development of his subject with a very readable series of sketches of the various branches of chemistry and their incidence in nature and in industry.

The book is well illustrated and the illustrations are chosen so that the casual reader, who at first is disinclined to serious study, is led to realise that here is much of interest which he can readily comprehend. Many will thus be tempted to know more ; if the appetite is still unsatisfied there is provided in an Appendix a fairly complete guide to the purchase of a chemical library. The reader who is led to study but a representative selection of this library, and to understand it, may thereupon and without contradiction call himself chemist.

This book is especially welcome in view of the various celebrations of the present year when the message of Science should be brought into the homes of all in this country.

A Textbook of Practical Physical Chemistry. By K. FAJANS and J. WÜST. Translated from the German by Bryan Topley, with a Preface by F. G. Donnan, LL.D., F.R.S. (London : Methuen & Co., Ltd., 1930. Pp. xv + 233. Price 15s. net.)

Professor Donnan states in his preface that the book covers a very wide field and is characterised by many highly commendable features. The theory is given in the case of each measurement, and such important matters as radioactive transformations, spectrophotometric measurements, ultra-violet spectrography, metallography, potentiometric titration, the quinhydrone electrode, etc., are included. The translation is good and the book is one which can be recommended as giving a sound course of practical physical chemistry covering all the experiments which are usually possible in the time available for the subject in a university laboratory.

Chemische Thermodynamik. Einführung in die Lehre von dem chemischen Affinitaten and Gleichgewichten. By HERMANN ULICH. (Dresden and Leipzig : Verlag von Theodor Steinkopff. 1930. Pp. xvi + 353. Price 18·50 R.M. or 20 R.M. bound.)

Dr. Ulich is known as a joint author of a comprehensive treatise on Thermodynamics which appeared last year (Schottky, Ulich and Wagner, Thermodynamik, Berlin, 1929), and the work which he did in the preparation of this treatise has made it possible for him to write a smaller and more elementary book on the same lines which is intended to serve the needs of chemists, physiologists and geologists who wish to make use of thermodynamic methods in their work. The treatment is adapted to such readers, stress being laid on clearness of exposition and close contact with numerical problems throughout. The symbols used are those of the larger treatise, and there is no doubt that in systematising the notation of the subject the author has made it difficult to fall into the pitfalls which some investigators have unfortunately not seen in using the notation of partial molar quantities. At the same time the large number of special symbols may at first sight prove rather confusing to English readers, since many of them are in German characters. There are, for example, ten different kinds of letter U, nine of letter S and eight of letter W, and some of these are very difficult to distinguish except when they occur together on a page, since in some cases only slight differences in size distinguish the different symbols. The three letters W shown on the top right-hand corner of p. xiv, for example, are not at all easy to distinguish in the text. The notation of Lewis and Randall, although less logical perhaps, is much easier to write, print and comprehend. This is a small matter and it is realised that the choice of a notation in chemical thermodynamics, where so many magnitudes are involved, is a matter of great difficulty.

The activity is used freely and the methods of Lewis and Randall are generally

followed, with some differences in detail.   The use of partial molar quantities and the corresponding coefficients is carefully explained, the equations being developed by strict methods and illustrated by well-chosen numerical examples.   The applications of the subject, in fact, take up about half the book, a feature which will make an appeal to the type of reader for whom it is intended.   The mathematical equipment assumed is of a very modest order and is practically confined to the notation of the calculus and a few simple applications.   One or two more difficult points are fully explained in foot-notes.   The book is very well printed and illustrated on excellent paper and is provided with a good index.   It may be recommended as a clear, accurate and practical account of modern thermo-dynamics suitable for students and investigators who may have occasion to apply that subject in their work.   The very practical treatment will also make the book useful to chemists engaged in the study of technical problems.

<div style="text-align: right">J. R. PARTINGTON.</div>

Applications of Interferometry.   By W. EWART WILLIAMS, M.Sc.   Pp. viii + 104.   F'scp. 8vo.   [Monographs on Physical Subjects, Messrs. Methuen & Co, London.]   Price 2s. 6d.

This volume makes a special appeal to physicists.   Physical chemists will be chiefly interested in the account of the improved forms of Rayleigh refractometer. Its accuracy is so high that even with the permanent gases the refractive indices of which are comparatively close, a displacement of $\frac{1}{20}$ fringe with 100 cm. chambers will occur when 0·01 per cent. of hydrogen is present as an impurity in air.   A similar displacement would be given by 0·006 per cent. of Helium and 0·0095 per cent. of carbon dioxide.   It is used in testing the permeability of balloon fabrics to hydrogen and the quantitative analysis of flue gases.   With shorter cells it can be used for testing the salinity of sea-water and the concentration of standard salt solutions.   In the biochemical examination of blood serum a special 1 mm. chamber has been employed.   The Haber-Löwe type of inter-ferometer is a portable type which can be strapped to the observer for the examination of mine gases.

A rapid survey is made of a great variety of interferometers with a discussion of the important parts of each in their application to terrestrial and celestial questions.   Mr. Williams has a practical knowledge of the subject and is himself responsible for some of the devices that are now on the market.

As for the other volumes in the series, it should be added that the book is not a primer but carries the subject beyond what is usually found in textbooks.

The Electrochemistry of Solutions.   By S. GLASSTONE.   (London : Methuen & Co. Ltd., 1930.   Pp. ix + 476.   (Price 21s. net.)

There has been for some years a need for a text-book on Electrochemistry on modern lines suitable for the student of chemistry proceeding to an honours degree, since the existing books, although excellent in many respects, fail to give those parts of the subject in which progress has been marked in recent years. In particular, the introduction of the conception of activity into the subject, and the consequent modifications in the treatment of concentration cells, for example, are not treated in sufficient detail for the requirements of students in the text-books on the subject, whilst the treatment in special works does not include the other parts of electrochemistry which are equally important.   Again, the subjects of over-voltage and polarisation are not usually dealt with from the modern standpoint.   Most teachers will no doubt have felt these difficulties and will have wished that a text-book on modern lines, sufficiently comprehensive for the type of student referred to, yet at the same time suitable for students who find difficulty

even with the simplest applications of higher mathematics (and there are many such among chemistry students), was available. It would seem to the reviewer that Dr. Glasstone has gone a long way towards the ideal text-book, even if he has not reached that perhaps unattainable goal, and there seems little doubt that his book is by far the best which has yet appeared on the subject in any language. It is not a mere compilation of material, since the subject is dealt with in a critical, whilst impartial, manner, and the evidence of careful and accurate thought is clear throughout. The activity is introduced fairly early in the treatment and is used when it is necessary to do so, the classical theory being applied in the numerous cases where it is still very approximately valid. All the usual topics appear, but in addition there are chapters on neutralisation and buffer action, indicators, amphoteric electrolytes, electrometric titration, over-voltage and passivity, to name a few examples, in which modern material not found in the usual text-books finds a treatment adequate for the purposes of the student. The references to the literature will prove useful to more advanced students and research workers, and for reference in technical laboratories. Dr. Glasstone is to be congratulated on producing a book which deserves to become popular, since it satisfies a distinct want. There are, naturally, some parts in which the reviewer would have preferred a different treatment. In particular, the expression of osmotic work as Vdp, although it has the sanction of Ostwald, seems unfortunate, since a work term is always pdV, however it may afterwards be modified by integration by parts. The idea that pdV and Vdp may be written indiscriminately for the external work is one which students should be taught to avoid, since it may involve the assumption of Boyle's law, whereas the student often jumps to the conclusion that it is general. It would perhaps be wiser in future editions to alter this treatment somewhat. The question of individual ion activity is one on which modern views differ, and some note might have been made of this. It is not certain that this concept will prove to be as useful as was at first assumed. The word "solvolysis," although it is coming into use, jars the nerves of anyone who thinks for a moment on derivation—but perhaps very few do. "Lysolysis" is not hybrid, and the duplication is not alien to the spirit of the language from which it is derived. In connection with the name "hydrogen ion," the time seems to have come to avoid ambiguity by a more complete nomenclature, since the "hydrogen ion" is different in different solvents. The use of such names as hydronol-hydrion, ethanol-hydrion, etc., would solve the difficulty. That the word "buffer" is a translation of the German "Puffer" may well be correct, but there seems no need so to explain a word which has long been well known in the sense used in English railway practice. Guggenheim's recent criticism of the use of flowing junctions should find a place in future editions, since it was too readily assumed that this type of junction had a great advantage over others. In connection with Billitzer's results (p. 288) it should have been mentioned that Garrison in 1923 claimed to have substantiated them. In discussing the hydrogen electrode as the standard of potential the author might have paused for a moment to consider whether, after all, it is the most suitable for the purpose, since its practical use is restricted by a number of considerations, *e.g.*, the reducing action of the electrode, whilst from the theoretical point of view the question of the equality or otherwise of hydrogen electrodes made up with different metals (on account of the different work functions for the liberation of electrons from the metals) might have been mentioned. One of the points which struck the attention of the reviewer was the number of references to the *Transactions* of the Faraday Society which are necessary in a modern work on Electrochemistry. It is clear that no worker on this subject can keep abreast of the times without this journal.

J. R. P.

AN AIR THERMOSTAT FOR QUANTITATIVE LABORATORY WORK.

By W. H. J. Vernon.

The work recorded in an accompanying paper on the study of atmospheric corrosion in the laboratory has depended largely upon the maintenance of a constant temperature over comparatively long periods. The use of an air thermostat for this purpose, dictated primarily by its greater convenience as compared with a water thermostat, has yielded, in fact, a higher degree of precision than was expected. In the early stages of the work a thermostat was constructed simply by the adaptation of a laboratory fume cupboard. The sides and sliding door of the cupboard were lagged with asbestos board ; in addition, an asbestos screen was placed immediately behind the door with an opening sufficiently large to admit the bell-jars used in the experiments. A toluene regulator of special design extended transversely across the middle of the cupboard. Connection was made to a relay of the " mercury cup " type ; later, two relays in parallel were employed with a third relay in series operated by a subsidiary regulator. The heating lamps were situated in the upper part of the cupboard in line with two fans, one at each end of the cupboard. During hot weather cold (tap) water was circulated through a length of " compo " tubing suspended between the fans, so that the normal working of the electrical control was ensured. This thermostat has yielded quite satisfactory results over a working period of more than two years. Owing principally to the limited capacity of the older cupboard, the construction of a new thermostat was undertaken some time ago, when opportunity was taken to introduce several features which experience with the modified fume-cupboard had shown to be desirable. As the thermostat can obviously be employed for purposes quite different from that for which it was originally designed, it is thought that a detailed description, accompanied by data obtained in actual use, may be of some general interest.

A description of an air thermostat designed for quantitative work is given in Clark's " Determination of Hydrogen Ions," [1] the arrangement of which was duly taken into account when the present work was commenced.[2] Quite recently a paper has been published by U. R. Evans [3] describing " an air thermostat for corrosion research." Evans' thermostat, whilst it has certain constructional features in common with the one to

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[1] 2nd edn., p. 233, 1923.
[2] The author is indebted to Dr. J. J. Fox for the opportunity of inspecting at the Government Laboratory, an air thermostat constructed according to the description given by Clark.
[3] *Chemistry and Industry*, **40**, 66, 1931. See also U. R. Evans, *ibid.*, p. 245.

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be described, introduces a novel principle, inasmuch as the actual thermo-stating of the air is conducted, not in the thermostat chamber itself, but in passages between the inner (metal) and outer (insulated) walls. No data are given whereby the performance of the thermostat can be adjudged; the experimental conditions would appear, however, to militate against uniformity of temperature within the walls and, hence, within the chamber. In the thermostat to be described, attention has been concentrated upon the symmetrical arrangement of the heating system and upon the symmetry and efficiency of the air circulation within the chamber itself.

Details of Thermostat Cupboard.

The thermostat was arranged to stand upon a laboratory wall-bench, the top of which is 34 ins. from the floor. The general arrangement of the cupboard and principal accessories is shown in elevation, longitudinal section, and plan (in each case drawn to scale) in Figs. 1 to 4. The external dimensions of the cupboard are 96 ins. long, 43 ins. high, and 39 ins. wide. The walls and roof are constructed externally of $\frac{1}{2}$-in. matchboard, backed by a lagging of compressed cork in closely fitting blocks, 2 ins. thick;[4] they are lined internally
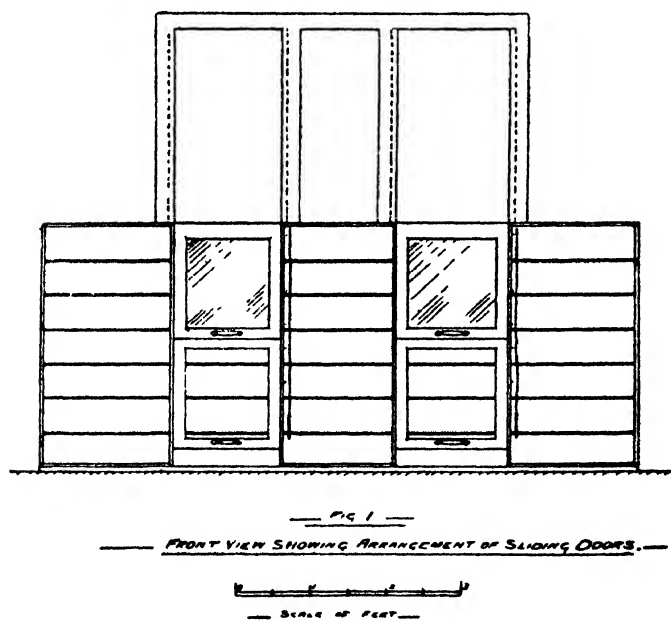
— FIG 1 —
FRONT VIEW SHOWING ARRANGEMENT OF SLIDING DOORS.—

— SCALE OF FEET—

with asbestos board $\frac{1}{4}$-in. thick. The two doors open by sliding vertically (a movement which is preferable to an outward movement with consequent danger of entrapping unthermostated air when the door is closed); each is in two parts, the upper of which fits by a dove-tail joint into the lower. The lower part is lagged with cork, whilst the upper part is fitted with two panes of glass, enclosing an air-gap as shown in section in Fig. 3. Either the upper part or the door as a whole can be fixed in a number of alternative positions by means of a peg (made from a 3-in. nail) engaging in a series of holes; in this way the opening can be reduced to the minimum required for any particular purpose. The top

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[4] E. Griffiths (D.S.I.R. Food Investigation Reports, Nos. 9 and 35) has shown that coarse granulated cork does not entirely suppress convection currents, and hence does not give such efficient insulation as slabs of the same material.

edge of the upper door is fitted with a rubber flap so that when the door is lowered the cupboard is completely closed.

The working floor is provided by a platform of 1-in. wood, between which and the base of the cupboard is a space of 3 ins. Between the platform and the inner walls there is a gap of $6\frac{1}{2}$ ins. at each end and 3 ins. at each side. There are also two square holes (4-in. edge, 9 ins.
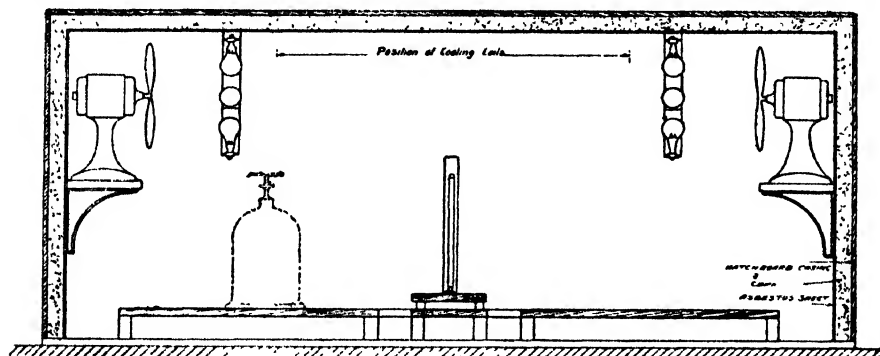
FIG 2 Longitudinal Section
(The positions of a ast jar as used in the main research is shown in dotted lines)
SCALE OF FEET

apart) in the platform itself, situated symmetrically about the middle. Between these holes, and extending transversely across the middle of the cupboard, is the main regulator (MR) to the rear of which is the subsidiary regulator (SR).

The main regulator (see Fig. 4) was designed with the object of obtaining maximum sensitivity. The bulb is made of $\frac{5}{8}$-in. glass tubing, and has a total length of 22 ft. ; it is bent into the form of a grid, 20 ins.
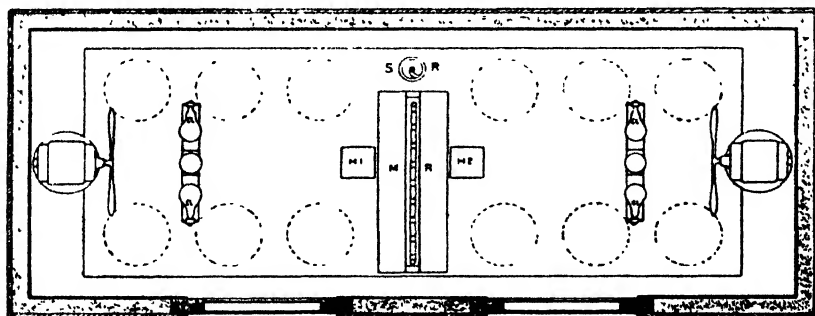
FIG 3 — Plan (Section Through Fans Heating Lamps, Windows)
(The sills of bell jars used in main research are shown in dotted lines.)
SCALE OF FEET

long by 15 ins. high, and comprises eighteen vertical columns. The column remote from the sealed end terminates 7 ins. from the base, at which point it is sealed to a vertical capillary tube of 1 mm. bore. The bulb tubes are filled with toluene, which has been kept in contact with mercury for several weeks with occasional shaking, followed by redistillation over sodium. The capillary tube (together with the first portion of the bulb tube, extending over the first lower bend) is filled with

mercury which has been cleaned and dried. The capillary tube terminates in the reservoir tube A, through the stopper of which is led a nichrome wire contact dipping at its lower end into the capillary tube and connected outside to a terminal on the wooden stand. The reservoir tube B communicates with the capillary tube by means of a side tube, and is provided with a stopcock by means of which a coarse adjustment of the mercury level is obtained. The arrangement [5] at C, which is shown in greater detail in Fig. 5, provides both the lower (permanent) mercury contact (thus avoiding a platinum seal) and also the fine adjustment. A small brass tube buts against a glass side tube leading into the capillary ; the tubes are of equal external diameter, and are secured end to end by a short piece of pressure tubing. The brass tube is provided with a collar on which is soldered a terminal, from which connection is made by a short length of wire to a stouter terminal on the wooden stand ; it is threaded internally and carries an iron screw, the inner end of which projects into the mercury contained in the side tube, the outer end being provided with a milled head whereby the level of the mercury may be adjusted with precision.

FIG. 4. TRANSVERSE SECTION THROUGH REGULATORS SHOWING HEATING LAMPS & FAN IN REAR.

The subsidiary regulator was not specially made for the purpose ; it is, however, a particularly sensitive type, the toluene bulb comprising a long spiral surrounding the central mercury capillary tube, with adjustable contact at the head of the tube.

Circulation of air is effected by two four-bladed fans, each 14 ins. in diameter, and each driven by a ball-bearing variable speed motor (Ediswan Ltd.). They are carried on brackets, one at each end of the cupboard, and their centres are 27 ins. above the level of the working

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[5] The arrangement described is a modified form of a fine-adjustment device provided by makers on certain types of regulator.

floor. The two opposing air streams, after passing over the heating lamps set in front of each fan, meet in the middle of the thermostat and pass downwards over the regulator bulbs. A portion of each stream passes through the corresponding hole (H_1 or H_2) in the working floor, under which it returns ; a portion is deflected to the sides of the cupboard and returns by way of the gap between the floor and the walls. The air in each half of the cupboard is thus effectively stirred, and is brought into rapidly repeated contact both with the heating lamps and with the regulator.

The heating lamps are of the usual carbon filament type ; they are arranged in two groups of four, each group being disposed symmetrically in a brass frame, which is suspended in front of the corresponding fan. The diameter of the frame (distance between opposite lamp-holders) is 15 ins. and the centre is in line with the centres of the fans. In each set of lamps only the two horizontal members (*e.g.* " CL " in Figs. 3 and 4) are controlled by the relays ; the other two (" AL ") are auxiliary lamps operated by switches outside. The four " control lamps " normally work in unison ; their heating capacity is arranged according to the outside temperature (with a mean room temperature of 16° and a thermostat temperature of 25°, a maximum of 32 c.p. is employed). In cold weather they may also be supplemented by one auxiliary lamp (8 c.p. in present practice) on each side, which is maintained permanently so long as the need lasts ; the criterion is that the " on " and " off " periods of the control lamps (the mean value of which under average conditions is approximately two seconds) should be approximately equal.

Fig 5 DETAILS OF LOWER MERCURY CONTACT & FINE-ADJUSTMENT ON MAIN REGULATOR (C IN FIG. 4)

If at any time it is necessary to open one of the doors widely, then another auxiliary lamp is switched on at the appropriate end of the cupboard, whilst the door is open, in order to compensate for local cooling and to maintain as far as possible the normal working of the system. As will be shown, the recovery from any such temporary disturbance is extremely rapid. For heating the thermostat rapidly from the cold to the desired working temperature, all the auxiliary lamps are employed.

Illumination of the cupboard, apart from that supplied by the heating lamps, is provided, on the usually quite temporary occasions when required, by a metal filament lamp situated at the centre of the ceiling.

During hot weather, provision is made for the circulation of cold water through a length of " compo " tubing situated just above the level of the control lamps, as shown in Fig. 2.

The relays (mounted outside the thermostat cupboard) are of the " mercury switch " type (Isenthal & Co.) capable of carrying a maximum current of four amperes.

Electrical Arrangements.

In the work for which the thermostat was primarily designed, it is of importance that the controlled temperature should be maintained

over long periods without risk of breakdown, even of a temporary character. Since the failure of a relay may result either in the heating circuit being permanently made or being permanently broken, the following system was introduced at an early stage in order to guard against either contingency.

Normally, the main regulator (MR, Fig. 6) works in conjunction with the two main relays (A and B) which are connected in parallel. If either of these fails in such a way that the heating circuit is broken, the other carries on at the temperature controlled by the main regulator. If, however, the failure of either A or B should result in the heating circuit being permanently made, the temperature would steadily rise, notwithstanding that its partner would cease to operate. The subsidiary relay (C), however, is arranged so that its heating circuit is in series with the heating circuits of A and B; it is operated by the subsidiary regulator (SR), which is adjusted to take control as soon as the temperature reaches a value very slightly higher than the normal working temperature. The margin of temperature may be adjusted to quite a small fraction of a degree and warning of the trouble is given by the subsidiary relay coming into operation.

FIG. 6. ELECTRICAL CONNECTIONS.

MR = Main Regulator.   SR = Subsidiary Regulator.
A & B = Main Relays   C = Subsidiary Relay
    m = Magnet Circuit Terminals
    h = Heating Circuit Terminals
    ⊹ = Condensers.

Sparking at the regulator head is eliminated partly by reducing the current in the magnet circuit to the minimum necessary to operate the relays, and partly by placing a condenser (2 microfarads capacity) across the regulator terminals. A similar condenser is also placed across the heating circuit terminals of the relays ; owing, however, to the much heavier currents, a certain amount of arcing still persists at the mercury surface, where the current is made and broken. In the mercury switch type of relay, in which the mercury is enclosed in a bulb containing hydrogen or inert gas, no harm can result from this residual arcing ; in the mercury cup type, fouling of the mercury may be largely prevented by the use of a covering of glycerine.

Performance of the Thermostat.

The thermostat was intended for regular use at a controlled temperature of 25° C., and the regulator was adjusted accordingly. At the outset, however, tests were conducted with the object of ascertaining the degree of control that it was capable of yielding, both with respect to constancy of temperature in point of space and constancy in point of time. Readings were taken with a Beckmann thermometer placed in turn in twelve different positions, corresponding with the positions of bell-jars to be used in subsequent experiments (see Fig. 3) and extending over the whole working space of the cupboard ; in each case the thermometer was left undisturbed for twenty minutes before the reading was taken.

The following results were obtained, the figures corresponding with the positions shown by the circles in Fig. 3 :—

2·675	2·680	2·690	2·690	2·680	2·675
2·675	2·680	2·690	2·690	2·685	2·680

The maximum spatial variation was thus 0·015°. During the progress of the tests the temperature immediately outside the thermostat varied between 17·5 and 19·5° ; variation of thermostat temperature in point of time during this period was no doubt negligible, because in a subsequent test, over a similar period, readings at twenty-minute intervals with the thermometer in a fixed position gave a maximum variation of 0·005°. This value (actually a rise in temperature following a succession of identical readings) was observed during a period when the front of the thermostat (including the two double-paned windows) was in direct sunlight so that the corresponding rise in temperature immediately outside the thermostat was 5·5° (17·0 to 22·5°). Readings were continued with the thermometer in the same position for two weeks after the thermostat had been put into regular use (during which time the outside temperature varied between 15·5 and 22·5°), but in no case, except for purely temporary disturbances caused by opening of the doors, was any greater deviation observed than 0·005°. The temporary nature of the disturbances referred to is shown by observations made on one occasion when one of the doors was open to its fullest extent for a period of three to four minutes with auxiliary lamps in operation ; during this time the temperature at the observation point fell 0·03°, but the normal reading on the Beckmann thermometer was resumed within twenty seconds of the closing of the door.

Summary.

Details are given of an air-thermostat designed with the object of maintaining accurate control of temperature over comparatively long periods. Readings on a Beckmann thermometer placed in different positions over the whole working space of the thermostat (the working floor of which measures 79 ins. × 30 ins.) showed a maximum " spatial variation " of 0·015° at a controlled temperature of 25° C Variations in point of time did not exceed 0·005° (observations extended over working period of two weeks, with thermometer in fixed position in thermostat ; outside temperature varied between 15·5 and 22·5°). A temporary disturbance caused by opening a door of the thermostat to its fullest extent for three or four minutes, resulting in the temperature falling by 0·03°, was completely eliminated in twenty seconds.

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THE QUANTITATIVE HUMIDIFICATION OF AIR IN LABORATORY EXPERIMENTS.

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At the outset of a research on the behaviour of metals toward various synthetic atmospheres, the first results from which are recorded in an accompanying communication, a method was sought whereby water vapour could be conveniently introduced into a given volume of air so as to produce an atmosphere of any desired relative humidity. The principal requirements were those of accuracy, rapidity, and freedom from contamination by any substance other than water vapour ; simplicity in operation (since the method was intended to be in constant use over a long period) and economy in space, were also desired. The results of this subsidiary investigation having presented what appears to be a sufficient number of points of interest, the results are now communicated as a supplementary paper.

A considerable amount of work has been published on the humidification of air, much of which, however, has been concerned with large-scale technical investigations employing methods which are not suited to the requirements of the present research. In small-scale laboratory experiments, humidification is usually effected by maintaining the air in contact with a solution of appropriate vapour pressure, either by confining the solution in the vessel containing the air, or by drawing the air in a steady stream through the solution. For reasons besides the unduly long time taken for equilibrium to be reached, either of these methods is precluded in the present work ; on the one hand, because the presence of liquid in the reaction vessel is obviously inadmissible, on the other hand, because of the risk of contaminating the air by spray carried from the solution. Another method, used successfully by Urquhart and Williams [1] is to admit the requisite amount of water vapour directly into the previously evacuated container. After tentative experiments, this method was abandoned owing mainly to the difficulty in controlling the operation and in checking experimentally the humidity that is actually developed. At an early stage it was decided to work upon the principle of admitting the requisite proportion of desiccated and saturated air into the reaction vessel.[2] This procedure, however, only raised the further problem of completely saturating a fairly rapid stream of air.

Experiments very soon showed that the simple method of bubbling air through a column of water is definitely inefficient. Reference to the literature revealed that the deficiencies of the bubbling method had

[1] *J. Textile Inst.*, 15, 433, 1924.
[2] A similar principle has been employed by other workers in other fields, *e.g.* M. H. Preston (unpublished thesis, through courtesy of Dr. G. F. New), Poole and Powell (*J. Soc. Chem. Ind*, 50,, 29T, 1930) ; Walker and Ernst (*Ind. & Eng. Chem. Anal. Ed.*, 2, 134, 1930). These papers (all of which came to the notice of the authors after their method had been worked out) are concerned, however, with the humidification of a continuous stream as distinct from a given volume of air ; on other grounds, moreover, the methods employed are not quite suited to the requirements of the present work.

already been pointed out, notably by Berkeley and Hartley [3] in their work on the measurement of the vapour pressure of solutions ; nevertheless, these deficiencies do not seem to be generally appreciated, and it is commonly assumed that air may be readily saturated by this simple method. Berkeley and Hartley attributed the unsatisfactory results obtained with a battery of vertical tubes (actual figures, however, were not recorded) mainly to variation in hydrostatic pressure ; they succeeded in eliminating error by passing the air over the liquid instead of through it, employing for this purpose specially devised horizontal saturating tubes to which an oscillatory motion was imparted. This method involved a very slow passage of the air stream, a determination of vapour pressure occupying at least two days. The method was improved upon by Pearce and Snow [4] (using horizontal saturators of a type described by Bichowsky and Storch [5]) by the adoption of pre-saturators, consisting of a battery of tubes in which the air is brought into equilibrium with water vapour a few degrees above that of the saturators themselves. In this way, the duration of experiments comparable with those of Berkeley and Hartley was reduced to little over an hour. Although admirably suited for its original purpose, however, the whole apparatus is inconveniently cumbersome for the conditions of the present research.

The method which was finally adopted consists in super-saturating the air stream by admission of steam, the excess of which is condensed out under thermostated conditions. The actual procedure will be described later. First, however, an account will be given of the arrangement employed for comparing the efficiencies of several methods of saturating air, to be followed by results obtained in the preliminary experiments with the " bubbling method."

Relative Efficiencies of Several Methods of Saturating Air.

Experimental.

A stream of air was obtained by aspirating air into an evacuated bell-jar of 1·88 litre capacity, enclosed in an air thermostat [6] at 25ᶜ. On its way to the bell-jar the air was led successively through (i) a purification train, (ii) the apparatus used for humidification, (iii) the absorption tubes for removal and determination of water vapour. The stream was maintained at an approximately constant rate by a tap on the bell-jar, the resistance of the train being overcome toward the end of the experiment by the application of a gentle stream of compressed air (pressure not exceeding 6 cm. of mercury as determined by a mercury " safety-valve tube " in series). Passage of air was continued until atmospheric pressure was reached in the bell-jar, as shown by a mercury barometer tube connected thereto. The time occupied by the passage of the air stream in each experiment was approximately ninety minutes, *i.e.* a rate of flow of approximately 1250 c.c. per hour ; this rate appeared to be as high as could be permitted without risk of inefficient absorption of water vapour in the tubes following the humidifying apparatus.

The purification train consisted of (i) a tower, 9 ins. high, packed with pure cotton wool for filtering out solid impurities, (ii) a similar tower charged with paraffin wax shavings (on glass wool) for removing any condensable organic compounds, (iii) three " Babo towers " con-

[3] *Proc. Roy. Soc.*, A, **77**, 156, 1906.   [4] *J. Physical Chem.*, **31**, 231, 1927.
[5] *J. Amer. Chem. Soc.*, **37**, 2696, 1915.
[6] This air-thermostat was the one used in the main investigation ; for description, see accompanying paper (this volume, p. 241).

taining glass beads, each tower charged with alkaline permanganate solution, (iv) a tower charged with flake caustic potash. Determinations showed that the relative humidity of the air on leaving the purification train was approximately 4·0 per cent.

In each method of humidification, saturation was effected at a temperature of 25°, for which purpose the appropriate apparatus was immersed in an electrically-controlled water thermostat, the temperature variation of which, under normal conditions, was less than 0·01°.

Two stoppered U tubes (length of limb, 11 cm.) each with bulb trap and each charged with glass beads, were used for absorption tubes. Phosphorus pentoxide was at first employed for the absorbing material but was abandoned, owing to the erratic " blanks " obtained, in favour of concentrated sulphuric acid (" analytical reagent "). The absorption tubes were contained in the air-thermostat together with the bell-jar. The short tube between the air-thermostat and the portion of the apparatus immersed in the water-thermostat was carefully lagged with asbestos string.

Weighings were conducted by the Conrady (oscillation) method, and were correct to within 0·01 mg. In weighing either absorption tube a similar tube was used as a counterpoise, and all other usual precautions were taken.

" Dreschel Wash Bottle " Method.

Columns of distilled water were contained in Dreschel wash bottles, each 4·2 cm. internal diameter ; the height of the column in a full bottle was 14 cm. Results of experiments employing half-filled and completely-filled bottles, in several different arrangements, are given in Table I.

TABLE I.—HUMIDIFICATION OF AIR BY PASSAGE THROUGH WATER CONTAINED IN DRESCHEL WASH BOTTLES.

	Number, Contents, and Arrangement of Bottles.				
	½. (Half-filled Bottle Only.)	1. (One Completely Filled Bottle.)	1 + ½.	½ + 1.	1 + 1.
Values obtained for relative humidity per cent.	75·4 76·3 76·7 76·7 75·6	81·8 81·8 82·1 81·9 82·3	78·6 78·1 78·7 78·7 78·8	86·0 89·9 87·0 85·0 86·4	88·6 87·8 — — —
Mean relative humidity	76·1	82·0	78·6	86·9	88·2

The anomalies to be observed are almost certainly due to variations in hydrostatic pressure. An interesting state of affairs is revealed by the third and fourth groups of results ; passage of air through two wash-bottles, one of which is completely filled and the other half-filled with water, results in a higher or lower relative humidity according as the smaller column of water precedes or follows the larger. Since the total hydrostatic pressure is the same in each case, the explanation most probably lies in the greater room for expansion (together with the greater surface of glass on which moisture may deposit) which obtains when the

air bubbles are liberated in the half-filled jar, following the compression which they experienced during their passage through the liquid. Other things being equal, as would be expected, the degree of saturation increases with the total depth of water traversed.

" Babo Tower " Method.

In the " Babo tower," more intimate contact between water and air is ensured by packing glass beads into the tube containing the water column. For the purpose of the experiments four Babo tubes were made, of dimensions which permitted their being immersed in the water thermostat ; the total length of each tube was 33 cm., of which 23 cm. was occupied by beads ; the internal diameter was 2·75 cm. ; the diameter of beads was 0·75 cm. Distilled water was introduced into each tube in sufficient quantity just to cover the beads whilst air was passing. The tubes were allowed to remain in the thermostat for at least two days before being used in an experiment. The time taken for the passage of air in the series of experiments varied from eighty-five to ninety-five minutes. The results obtained from various combinations of tubes are given in Table II.

TABLE II.—Humidification of Air by Passage through Water Contained in Babo Tubes.

	Number of Tubes in Series.				
	Tube without Beads	Tubes with Beads.			
	I.	I.	2.	3.	4.
Relative humidity values.	67·8 70·0 67·8	---- 83·3 82·5	--- 85·0 85·3	—— 86·1 86·2	—— 95·3 95·6
Mean relative humidity.	68·5	82·9	85·1	86·1	95·5

In order to determine the precise influence of the beads, a tube was included having the same dimensions as those used in the main tests, and containing the same quantity of water, but containing no beads ; the height of the water column in this tube was 9 cm. The mean relative humidity obtained by passing air through the plain tube was 68·5 per cent , as compared with 82·9 per cent., employing a tube packed with beads. Comparing the behaviour of the tubes in series, there is a definite increase in relative humidity with increasing number of tubes. Presumably, the relative humidity would increase asymptotically with a still larger number of tubes ; in view, however, of the cumbersome nature of a battery of such tubes, together with the large (total) head of water to be overcome, the method leaves much to be desired.

" Steam " Method.

The arrangement of apparatus in the method whereby steam is introduced into the air stream is shown in Fig. 1. The boiling flask A is

of hard glass, with sealed-in connections; water is introduced and re-plenished when necessary, through a funnel attached to the tap *f*. Air from the purification train is admitted at *e*. After leaving the reflux condenser B, the mixture of air and water vapour enters the glass bulb trap C, which is immersed in the water thermostat at 25°, and in which practically all the excess of water vapour condenses. (The tube *g*, with tap, is for the purpose of removing accumulated water, usually at the end of each run.) Equilibrium is completed in a long length of thin-walled glass tubing (internal diameter 0·4 cm.) bent into the form of a grid; this is represented at D in Fig. 1, but schematically only.[7] Actu-ally, there are two similar grids side by side, each measuring 20 by 12 ins., and each supported on a copper frame running the whole length of the thermostat; they are connected in series and comprise a total length of approximately 75 ft., which is probably in generous excess of the length actually needed for efficient thermostating. During an experi-
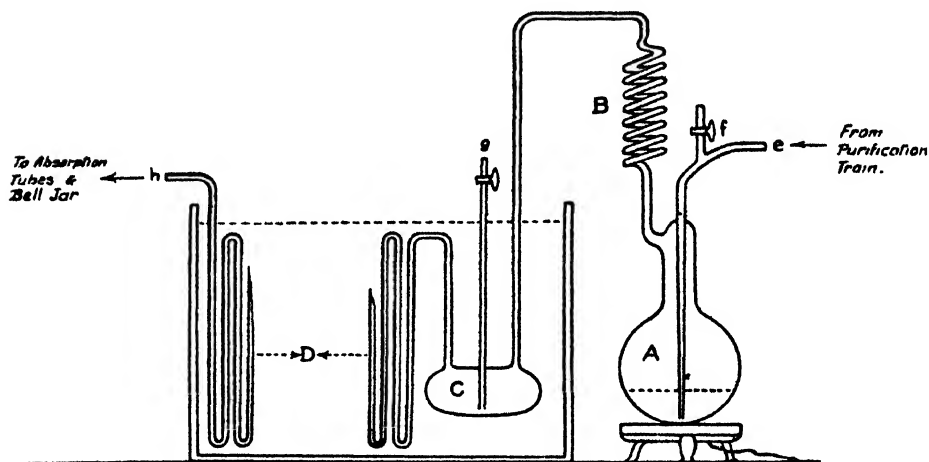
FIG. 1 .

Arrangement of apparatus used for saturating air by 'Steam Method.'

ment a slow stream of cold tap water is circulated through a " compo ' tube in the vicinity of the bulb trap in order to compensate for the addi-tional heat carried into the thermostat; in this way the normal working of the electrical control is ensured and the temperature in the neigh-bourhood of the grid is maintained constant to within $\pm$ 0·01°. From the grid the air stream passes to the absorption tubes and bell-jar (in ordinary practice the absorption tubes, are of course, omitted); the short length of connecting tube between the grid and the air-thermostat is lagged with a double layer of asbestos string.

Three typical results are given below :—

(1) Increase in weight of absorption tube = 0·04228 gram.
   ,, ,, ,, guard ,, = 0·00057 ,,

   Total weight-increment   = 0·04285 ,,

[7] The arrangement is shown more clearly in plan in Fig. 2.

Per Cent.

Relative humidity[8] $= 42.85 \times \left(\dfrac{100}{22.8 \times 1.88}\right) = 99.9$

(2)   „   „ $= 43.07 \times 2.33$ $= 100.5$
(3)   „   „ $= 42.90 \times 2.33$ $= 100.1$

It will be seen that the method satisfactorily meets the requirements enumerated at the outset in respect to efficiency, freedom from contamination, compactness, ease of operation and rapidity. In ordinary practice the duration of an experiment is dictated by the rate at which the air stream can be safely passed through the purification train; in the main research a period of three to three-and-a-half hours is taken in filling a bell-jar of 10 litres capacity, i.e. a rate of flow of approximately 3 litres per hour. In order to ascertain whether the method is equally reliable at the higher speed of working, two experiments were carried out in which this speed was realised, the time occupied in filling the small (1·88 litre) bell-jar being thirty-five minutes, as compared with ninety minutes in the previous experiments; the results are given below:

(1) Increase in weight of absorption tube = 0·040802 gram.
 „   „   guard   „   = 0·002268   „

Total weight-increment   = 0·043070   „

Relative humidity = $43.07 \times 2.33 = 100.5$ per cent.
(2)   „   „   = $42.92 \times 2.33 = 100.1$ „

Clearly, the great increase in speed (more than double that employed in previous experiments) is without influence upon the efficiency of the saturation.

Preparation of Atmospheres of Intermediate Humidities.

The problem of obtaining a supply of completely saturated air under thermostated conditions having been satisfactorily settled, the prepara-
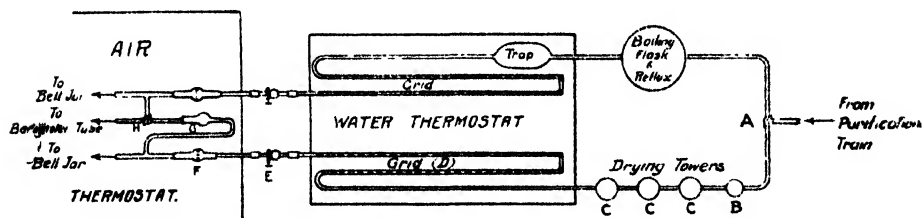
FIG. 2

Arrangement of apparatus for preparing atmospheres of definite relative humidities.

tion of atmospheres of intermediate humidities was quite straightforward. The procedure was simply to admit the requisite amount of desiccated air, as indicated by the barometer tube connected with the evacuated bell-jar, and then to complete the filling of the vessel in the manner already described. The arrangement of apparatus is shown in plan in Fig. 2. Connection alternatively to the saturating branch (the essential features

*Volume of air employed in experiment is 1·88 litre; saturated air at 25° contains 22·8 mg. water vapour per litre (Regnault's value).

of which have already been discussed) or to the desiccating branch is effected by the three-way tap A.   Desiccation is effected by passing the air stream, first through a Dreschel wash-bottle (B) charged with concentrated sulphuric acid on glass wool, finally through three towers (C) charged with phosphorus pentoxide on glass beads (length of each tower actually occupied by drying material is 15 cm. ;   internal diameter of tower, 4·5 cm.).   From the drying tubes the air passes to the grid (D) which is exactly similar to the grid in the saturating branch, and is similarly immersed in the water thermostat.   There follows next a fine-adjustment metal tap (E) whereby the regulation of the rate of flow is greatly facilitated.   Between this tap and the bell-jar (or the absorption tubes in the case of the experiments recorded below) there is interposed a Jena glass filter tube (F) for the purpose of intercepting any solid particles which might be carried from the drying train.   Both the regulating tap and the filter-tubes are duplicated in the saturating branch, as shown in the diagram ;   the connecting tubes between the water-thermostat and the air-thermostat are lagged with a double layer of asbestos string. Inside the air-thermostat, at a point immediately preceding the bell-jar, the two branches are connected by a three-way tap H, whereby either branch (according to which is in series with the bell-jar) can be put into connection with the barometer tube.   Whilst the saturated stream is passing, saturated air necessarily enters the barometer tube ;   although the system is evacuated before the next dry stream is passed, in order to avoid any possibility of water vapour diffusing from the barometer tube, a drying tube (G) charged with phosphorus pentoxide is interposed between the tap H and the delivery-tube conveying the desiccated stream.

Typical results for nominal relative humidities of 50 per cent. and 75 per cent. respectively are given below.   The total time taken for each of these experiments was approximately ninety minutes, as in the main series already recorded.

50 *Per Cent. Relative Humidity.*
(1) Relative humidity = 21·47 × 2·33 = 50·1 per cent.
(2)   ,,   ,,   = 21·83 × 2·33 = 50·9   ,,

75 *Per Cent. Relative Humidity.*
(1) Relative humidity = 32·0 × 2·33   = 74·6   ,,
(2)   ,,   ,,   = 32·03 × 2·33 = 74·7   ,,

Summary.

A method has been worked out for the preparation of atmospheres of any desired relative humidity.   The method depends upon admitting the requisite proportions of desiccated and saturated air into a previously evacuated vessel.   Several methods of saturating air have been investigated.   Passage of air through vertical columns of water was found to be definitely inefficient ;   anomalous results were obtained with partially-filled vessels.   Complete saturation was rapidly effected by the admission of steam into the air-stream and condensing out the excess under thermostated conditions.   Quantitative results at various relative humidities are recorded.

spheric corrosion of metals for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research. The thanks of the authors are due to Professor Sir Harold Carpenter, F.R.S., Chairman of the Committee and to Professor G. T. Morgan, F.R.S., Director of Chemical Research, for facilities afforded and for permission to publish.

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A LABORATORY STUDY OF THE ATMOSPHERIC CORROSION OF METALS.

PART I.—THE CORROSION OF COPPER IN CERTAIN SYNTHETIC ATMOSPHERES, WITH PARTICULAR REFERENCE TO THE INFLUENCE OF SULPHUR DIOXIDE IN AIR OF VARIOUS RELATIVE HUMIDITIES.

BY W. H. J. VERNON.

The results of a previous series of investigations on the atmospheric corrosion of metals have been communicated to the Faraday Society in the form of three reports to the Atmospheric Corrosion Research Committee of the British Non-Ferrous Metals Research Association, under whose auspices the work was conducted. The first two reports,[1] for which the present author was responsible, were concerned with the systematic examination of the behaviour of the common metals on exposure to several types of indoor atmosphere and to the open air ; in particular, the properties of thin (sometimes invisible) films of reaction product were studied, and their influence in determining the rate of attack was established. Methods of determining the rate of attack included measurement of loss of reflectivity and of change in weight, supplemented by micrographic examination and analysis of the products of corrosion, including, in the case of open air exposure, both the residual (" surrosion ") product adhering to the metal, and the soluble (" erosion ") product removed by rain.

The Third Report,[2] by Dr. J. C. Hudson, was concerned exclusively with field tests in the open air and recorded the results (after a period of exposure, in most cases, of twelve months) of a comprehensive series of tests on a wide range of non-ferrous metals and alloys, at five representative stations in this country. For the purpose of these tests Hudson developed a method whereby the change in electrical resistance of thin wires was utilised as a measure of the rate of corrosion ; this was supplemented by determinations of changes in weight, by micrographic examination, and by tensile tests ; the results of the tensile test experiments have been published as a separate and later communication.[3]

Since the publication of the Second Report, the open air corrosion of copper has been dealt with in two papers[4] by the present author, in collaboration with Mr. L. Whitby, chiefly from the point of view of the

[1] *Trans. Faraday Soc.,* 19, 839, 1924 ; 23, 113, 1927.
[2] *Ibid.,* 25, 177, 1929.   [3] *J. Inst. Metals,* 44, 409, 1930.
[4] *Ibid.,* 42, 181, 1929 ; 44, 389, 1930.

composition of the green patina that characterises copper surfaces after prolonged exposure.[5]

All the foregoing communications have one characteristic in common, in that they deal with the behaviour of the metal during exposure to ordinary everyday atmospheres. In connection with the First and Second Reports, some work was done with the object of associating certain effects with specific atmospheric constituents ; for the most part, however, the experiments were " analytic " in character, *i.e.* they depended upon the *removal* of the constituent under investigation. Experiments in which additions were made to an otherwise pure atmosphere (*i.e.* the "synthetic" method) were admittedly limited, and the opinion was expressed that " much more work remains to be done in the field represented by these experiments." It is with the object of exploring this field, and more particularly with the object of investigating atmospheric corrosion under strictly defined conditions in the laboratory, that the present series of investigations has been instituted. The subject is thus approached from an entirely different angle from that represented in the previous researches. Instead of taking atmospheres as they are found, subject to the usual fluctuations in meteorological conditions, atmospheres will be prepared synthetically, and will be subjected to rigorous control with respect to composition, temperature, and relative humidity ; in this way, it will be possible to investigate one factor whilst others are kept constant.

In the present communication a technique is described which it is hoped will form the basis of an extended programme of research. The earlier investigations, whilst they did not altogether neglect the corrosion of iron, necessarily had a non-ferrous bias. Although this bias no longer obtains, it has been thought expedient to conduct the first series of experiments upon copper, more especially as it was desired to throw further light upon recent results obtained in the study of the open air corrosion of that metal. Synthetic atmospheres have been employed containing various concentrations of sulphur dioxide at various controlled relative humidities. Besides the main experiments at constant temperature, other experiments have been included to represent " supersaturated " conditions at fluctuating temperatures. The effect of carbon dioxide, and to a lesser extent hydrogen chloride, has also been investigated.

Experimental.

General Procedure.—The main experiments have dealt with the behaviour of copper towards atmospheres in which definite amounts of sulphur dioxide and of water vapour have been added to purified air ; concentrations of sulphur dioxide of 0·01, 0·1, 0·5, 1·0, 2·0 and 10·0 per cent. ; and relative humidities of 50, 63, 75, 99 and 100 per cent. at a uniform temperature of 25° C., have been investigated. Other experiments in which these conditions have been departed from in respect to the nature of the added constituent, temperature, hygrometric conditions, or purity of the metal, will be noted in their appropriate place.

An experiment consists normally in exposing eight small copper specimens to the atmosphere under investigation, in a bell-jar which is

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[5] The predominant constituent was found to be basic copper sulphate, except under purely marine conditions, when basic copper chloride predominated ; basic copper carbonate was present only in minor proportion. Complete agreement with the formula of the corresponding mineral (*e.g.*, Brochantite, $CuSO_4 . 3Cu(OH)_2$) was found in products after 70 years' exposure and upwards ; after shorter periods the basicity of the product was less than that of the mineral.

itself contained in an air-thermostat at 25°. At intervals, the atmosphere is replenished and, usually, a specimen is replaced at the same time. Typical intervals are as follows: 1, 4, 7, 11, 15, 20, 25, and 30 days. After the first withdrawal (when a similarly-treated specimen is added) each specimen is replaced by the one previously removed, so that the full complement is maintained. Between the removal of a specimen and its replacement its weight-increment is determined; the rate of attack is thus measured by the rate of formation of the corrosion product and a time corrosion curve is plotted for each experiment.[6]

Specimens.—Square specimens of 5 cm. edge (*i.e.* total area 0·5 sq. dm.) cut accurately to dimensions, with a single hole (0·3 mm. diam.) for suspension, have been used throughout the experiments. Unless otherwise stated, they have been taken from high-grade electrolytic copper sheet, 0·53 mm. in thickness; in some cases, for the purpose of comparison, similar specimens of arsenical copper, of B.E.S.A. specification, containing 0·45 per cent. arsenic, have been employed. The sheet has first been polished for the purpose of removing all surface defects; the final surface has been obtained by polishing each specimen separately with Hubert No. 1 emery paper; this has been followed by rubbing with pure cotton wool and, finally, immersion in pure carbon tetrachloride for removal of traces of grease. The specimens have then been transferred to a vacuum desiccator in which, after immediately evacuating, they have been allowed to remain overnight for weighing and exposure the following day.

Weighing.—The system of weighing employed throughout is based upon the work of Conrady [7]; this permits of specimens employed in the investigation (average weight 11 grams) being weighed correct to 0·001 mgm. In most cases this degree of accuracy has not been required, since the maximum error has been imposed in other ways; nevertheless, the specimens have usually been weighed correct to 0·01 mgm.

Suspension of Specimens.—The specimens in any given experiment are suspended on a stand constructed of glass rod (see Fig. 1). This carries eight projecting arms in two rows of four, each arm terminating in a hook from which the specimen is directly suspended; opposite specimens are 10·0 cm. apart. The arms are staggered, so that a specimen in the upper row is immediately over a gap between two specimens in the lower row. The specimens are placed on the stand immediately after weighing and the full complement is transferred to the bell-jar to be used in the experiment; this is at once evacuated and placed in position in the air-thermostat in readiness for filling with the atmosphere under investigation.

Bell-Jar and Accessories.—Each bell-jar (see Fig. 1) has a capacity of approximately 10,000 c.c.; height, approximately 14 ins.; internal diameter, 8¼ ins.; the base-plate is of thoroughly annealed glass, ½ in. in thickness, underneath which is placed a rubber mat ¼ in. in thickness. The stopper is fitted with a three-way tap; one of the side tubes is of normal diameter and is for the purpose of connecting to the air-pump for rapid evacuation; the other is of capillary (1 mm.) bore, and is for the purpose of connecting to the appropriate apparatus for filling. A mixture of vaseline and graphite is used as lubricant, vaseline having no dele-

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[6] Each curve given in the paper has been checked by means of at least one duplicate experiment. The degree of reproducibility is shown by typical figures in Table I. (Appendix), p. 274.

[7] *Proc. Roy. Soc.*, 101A, 211, 1922.

terious influence upon the composition of the atmosphere, whilst graphite prevents any seizing of surfaces under pressure.

The air-pump is a " Cenco Hyvac " pump, capable of giving a vacuum of 0·001 mm.

Preparation and Introduction of Atmosphere.—The development of a suitable method of preparing atmospheres of any desired relative humidity is dealt with in a supplementary paper [8] to which reference may be made for more precise details. The air is first led through a purification train in which incidental impurities are removed, together with, it should be noted, the whole of the normal content of carbon dioxide. It next passes alternatively, either through a desiccating train (a tower of concentrated sulphuric acid followed by three towers of phosphorus pentoxide) or through the saturating apparatus. From this point each branch is similar, and includes a long " grid " of
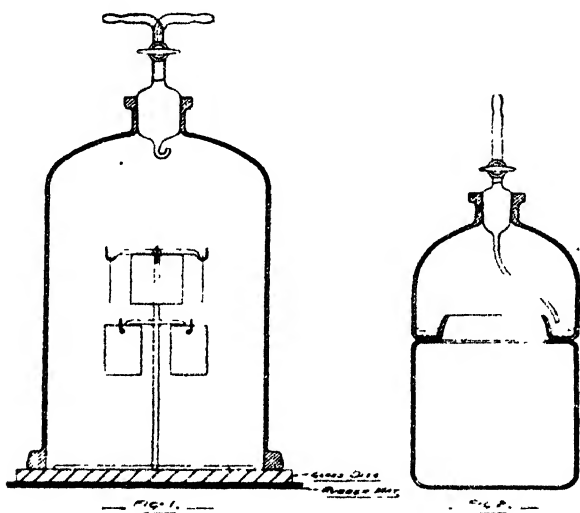
— CORROSION VESSELS USED ...

— FIG. I. — BELL JAR USED FOR ... SYNTHETIC ATMOSPHERES ...
SHOWING STAND WITH SPECIMENS IN POSITION.

— FIG. 2. — MODIFIED HEMPEL DESICCATOR USED FOR ... SATURATED ATMOSPHERES —

glass tubing immersed in a water thermostat at 25° (in which the air-stream is thoroughly thermostated), a fine-adjustment metal tap for regulating the rate of flow, and finally (inside the air-thermostat) a Jena glass filter tube, from which connection is made to the bell-jar. At this point the two branches are connected by a three-way tap whereby either branch may be put into communication both with the bell-jar and with a mercury barometer tube.

The evacuated bell-jar containing the specimens having been allowed to remain sufficiently long in the air-thermostat, the appropriate amount of dry air is admitted, as noted by the reading on the barometer tube, so that when the filling is completed with saturated air the desired relative humidity is obtained. Whilst there is still a negative pressure in the bell-jar of approximately 6 cm., passage of air is suspended whilst the addition is made, from a Hempel burette, of a mixture containing the

[8] " The Quantitative Humidification of Air in Laboratory Experiments." This volume, p. 248.

appropriate amount of special constituent (usually sulphur dioxide) or constituents necessary to bring the composition of the atmosphere in the bell-jar to that desired. This mixture is previously prepared in a separate bell-jar using (normally) pure dry air ; the sulphur dioxide is obtained from a syphon, and is either passed through several tubes containing phosphorus pentoxide or bubbled through water at 25° in the case of a completely saturated atmosphere. The mixture is brought to atmospheric pressure after standing in the air-thermostat, and the pressure of the withdrawn portion (usually 100 c.c. in volume) is adjusted in the Hempel burette before being added to the main bell-jar. Passage of the saturated stream (or the desiccated stream in the case of an atmosphere of zero humidity) is then resumed until the pressure in the bell-jar has reached atmospheric. Experience has shown that the diffusion of sulphur dioxide, or other gas, when introduced in this way into the partially evacuated bell-jar is extremely rapid.[9]

Air-Thermostat.—The two air-thermostats that have been used in the course of the research are described in a supplementary paper [10] ; the temperature control in the later of these is such that the maximum variation in point of time is less than 0·01° in several weeks, whilst spatial variation over the working space of the cupboard does not exceed 0·015°. The position of a bell-jar in the thermostat is shown in elevation in Fig. 2 (supplementary paper, p. 243). The delivery tubes from the humidifying apparatus are not shown in the diagram ; actually these extend right across the cupboard, so that a bell-jar may be filled on either side of the regulator, connection being made either to the desiccating or saturating branch by means of a side tube with stop-cock. The positions of a full complement of twelve bell-jars are shown in plan in Fig. 3 (supplementary paper, p. 243).

DISCUSSION OF RESULTS.

1. Unsaturated Atmospheres.

A. Atmospheres Containing no Added Impurity.—Experiments in which copper specimens were exposed to purified air, in the desiccated and saturated condition respectively, for periods up to forty days, revealed no visible change upon the metal. Gravimetric results are plotted in Fig. 3 (*curves A and B only*). In the case of the dry atmosphere the true values are excessively small and experimental error has naturally its greatest effect. A definite weight-increment was invariably obtained after one day's exposure, but no further measurable change was observed during the period of the experiment. The curve (A) is plotted according to the maximum values obtained, and represents a weight-increment of 0·015 mg. (actual) or 0·03 mg. per sq. dm. In the light of previous work,[11] in which a study was made of the oxidation of copper at temperatures above, but not far removed from normal (the values thus permitting extrapolation) this figure is in appreciable excess of the true value and the difference must therefore represent experimental error ; nevertheless, considering the series of experiments as a whole this curve may be accepted as the " datum " curve—any

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[9] See, for example, results obtained with hydrogen sulphide. Appendix, Table II., p. 275.

[10] " An air thermostat for quantitative laboratory work "; p. 241.

[11] W. H. J. Vernon, *J. Chem. Soc.*, 128, 2273, 1926.

departure from which may be definitely attributed to the conditions imposed in the particular experiment.

Curve B in Fig. 3 represents the action of purified air at relative humidities of both 99 and 100 per cent. relative humidity, complete saturation bringing about no measurable difference as compared with conditions just below saturation. There is, however, an appreciable difference between the action of these atmospheres and that of the desiccated atmospheres, corresponding with an increase in the weight-increment of 0·05 mg. per sq. dm.

B. Atmospheres Containing Sulphur Dioxide. — Atmospheres containing sulphur dioxide in concentration ranging from 0·01 to 10·0
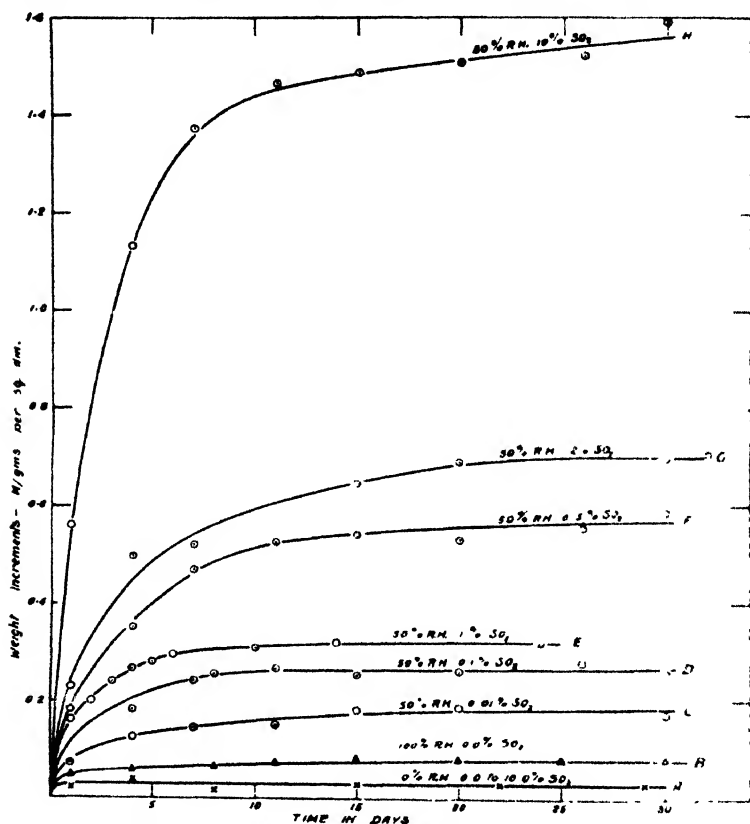
FIG 3.   Curve A. Atmospheres of Zero Relative Humidity (0·01 to 10·0 per cent. SO₂)
Curve B. Atmosphere of 100% Relative Humidity (0·0 per cent. SO₂)
Curve C. All Atmospheres of 50% Relative Humidity (0·01 to 10·0 per cent. SO₂)

per cent. have been investigated. The results are discussed in three groups, according to the relative humidity of the atmosphere.

(i) *Atmospheres of Zero Relative Humidity.*—Exposure to desiccated atmospheres, at all concentrations of sulphur dioxide, has had no visible effect upon the metal ; systematic weighings have also failed to show any effect due to the presence of sulphur dioxide, even at the highest concentration. The curve representing the action of these atmospheres is thus identical with the " datum " curve for pure dry air (curve A in Fig. 3).

(ii) *Atmospheres of 50 per cent. Relative Humidity.*—The introduction

of water vapour brings about an immediate differentiation among the atmospheres of various concentrations of sulphur dioxide, in respect to their action upon copper. This is shown in Fig. 3, where curves C to H represent the effects of atmospheres of 50 per cent. relative humidity, at the respective concentrations of sulphur dioxide. The curves are all similar in type, being exponential in form over the first part, and then " flattening " toward the time axis. The exponential portion persists for the longer time the higher the concentration of sulphur dioxide, but the (approximate) equilibrium value, represented by the nearly horizontal portion of the curve, is reached in all cases after about thirty days' exposure.

In Fig. 4 the various equilibrium values are plotted against concentration of sulphur dioxide. Whilst there is a general increase in corrosivity with increasing concentration, there is a marked break in the

Fig. 4

Relation between Corrosion & Concentration of SO₂ in atmosphere at 50% Relative Humidity
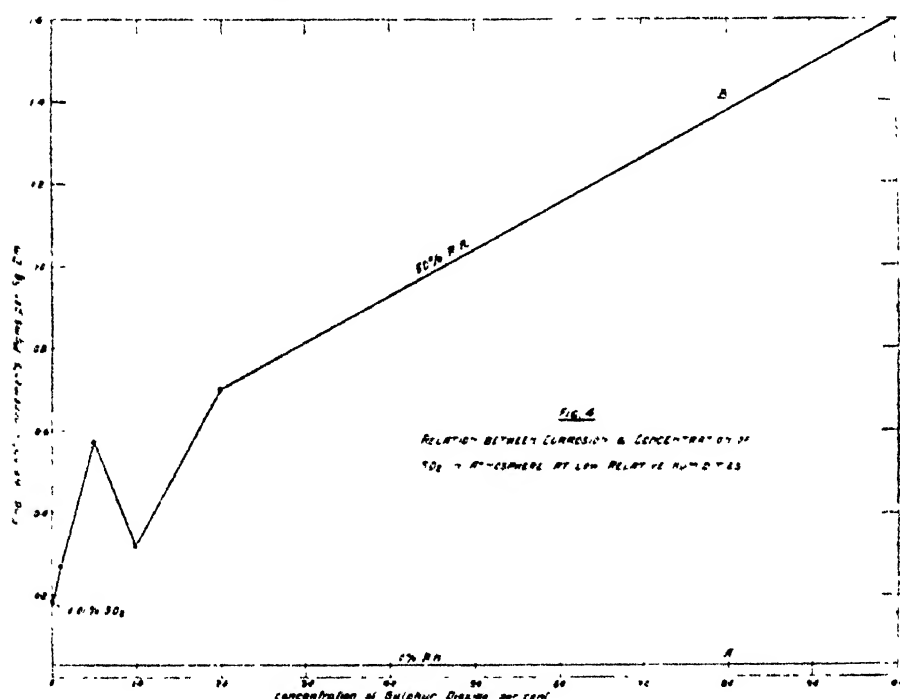
curve toward a minimum corrosion value at a concentration of 1·0 per cent. sulphur dioxide. This break will be referred to later in discussing the higher relative humidities.

All the corrosion values at 50 per cent. relative humidity (Figs. 3 and 4) are of a relatively low order, the specimens undergoing no more than a slight darkening after thirty days' exposure.

(iii) *Atmospheres of* 75, 99, 100 *per cent. Relative Humidity.*—At relative humidities of 75 per cent. and upwards the rate of attack is of a definitely higher order of magnitude than is the case with the atmospheres of 50 per cent. R.H. Accordingly, in Figs. 5 to 10, where the corrosion-time curves are grouped according to the sulphur dioxide content, a smaller vertical scale (equal to 1-50th that in Fig. 3) is employed. In each case, the curve for 50 per cent. R.H. is repeated, so that the difference in scale may be appreciated. The curves are similar in type

to those representing the lower rates of attack, except that a rather longer time (usually from thirty to forty days) is taken for the nearly flat portion to be reached. The appearance of the specimens after exposure varies from a darkening or clouding of the surface at the lower rates of attack to a definite coating of bluish corrosion product in the more corrosive atmospheres. At the highest rate of attack (10 per cent.
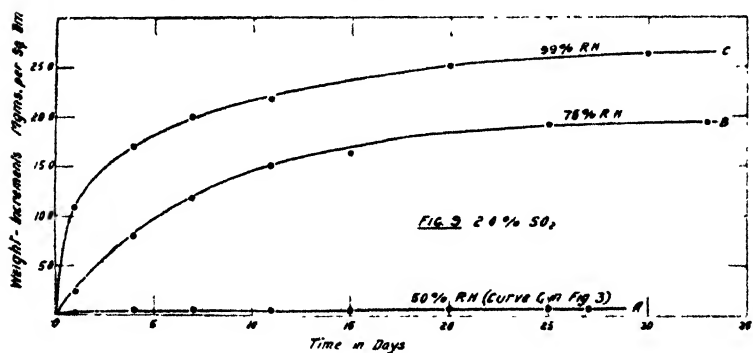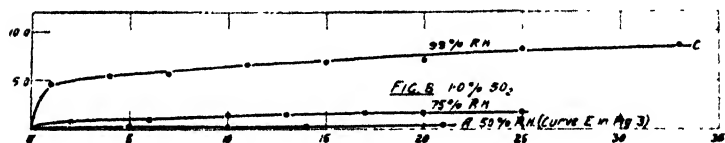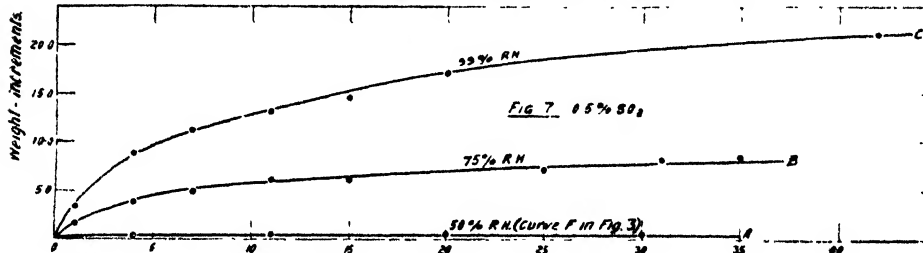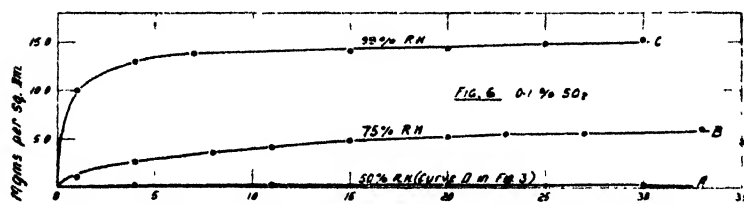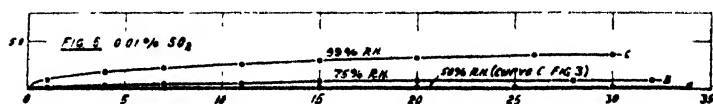
sulphur dioxide, 100 per cent. R.H.) the characteristic clouding of the surface is observed within ten minutes from the start; the specimen is appreciably attacked after a day's exposure (when traces of sulphate appear) and in the course of a week is covered with a bluish film. In cases where a comparison has been made between the action of atmospheres of 99 and 100 per cent. R.H., no difference whatever has been

observed in the appearance of the specimens, whilst any difference in weight-increment has been extremely small. In the case of the atmosphere containing 10 per cent. sulphur dioxide the influence of 63 per cent. relative humidity was investigated. In appearance after exposure the specimens from atmospheres of 50 per cent. and 63 per cent. relative humidity are indistinguishable; the difference gravimetrically (see curves A and B, Fig. 10) is also extremely small. There is, however, a relatively enormous difference between the effects of the atmospheres of 63 per cent. and 75 per cent. relative humidity.

FIG. 10 10% SO₂
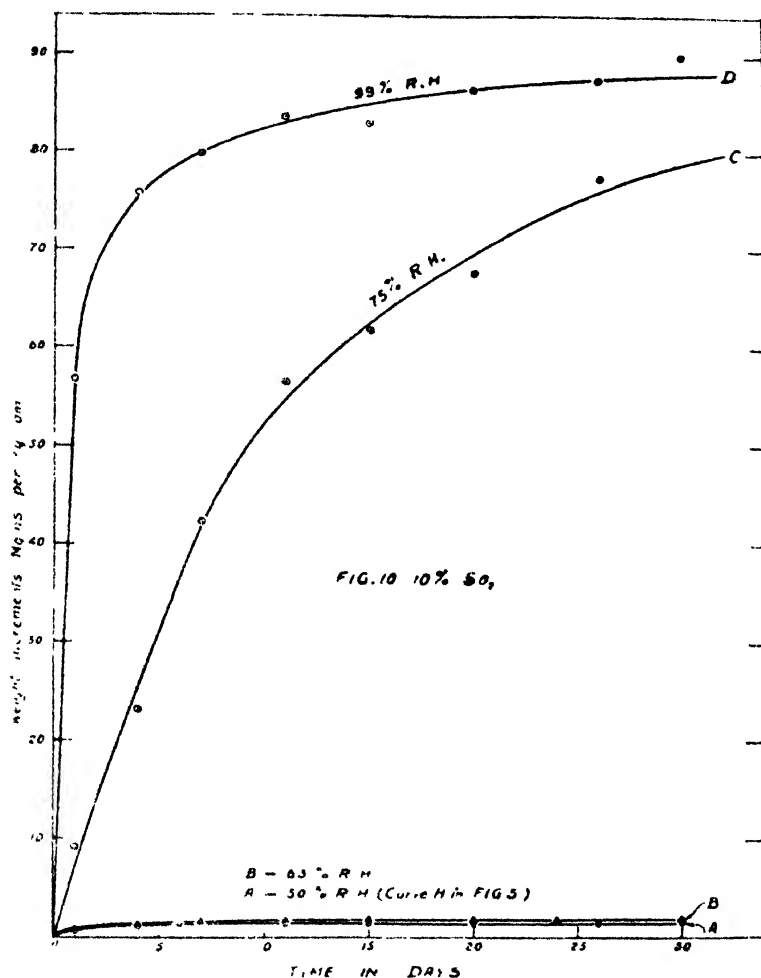
In Fig. 11, the final weight-increments, representing the nearly horizontal portion of each corrosion-time curve, are plotted against concentration of sulphur dioxide. Values for 99 per cent. and 75 per cent. R.H. are represented in the two main curves; values for 50 per cent. R.H. (plotted to larger scale in Fig. 4) are again included for comparison. Although atmospheres of 63 per cent. relative humidity are represented only at the highest concentration of sulphur dioxide, there is little doubt that the close proximity to the 50 per cent. R.H. curve would also

obtain at intermediate concentrations. Two points of major interest are represented by these curves. First, the great disparity between the effects of atmospheres of 50 and 63 per cent. and those of 75 and 99 per cent. relative humidity. The results point clearly to the existence of a *critical humidity* lying between 63 per cent. and 75 per cent., below which relative humidity has comparatively little, and above which it has a profound effect. Below the critical humidity, even at high concentrations of sulphur dioxide, specimens may be exposed without undergoing appreciable attack beyond a slight general darkening ; above the critical humidity the metal undergoes relatively severe corrosion at a rate which increases greatly with increasing concentration of sulphur dioxide. The conception of critical humidity was introduced in the Second Report [12] in connection with experiments upon the atmospheric

FIG II.

Relation between Corrosion & Concentration of SO_2 in atmospheres of high relative humidity.
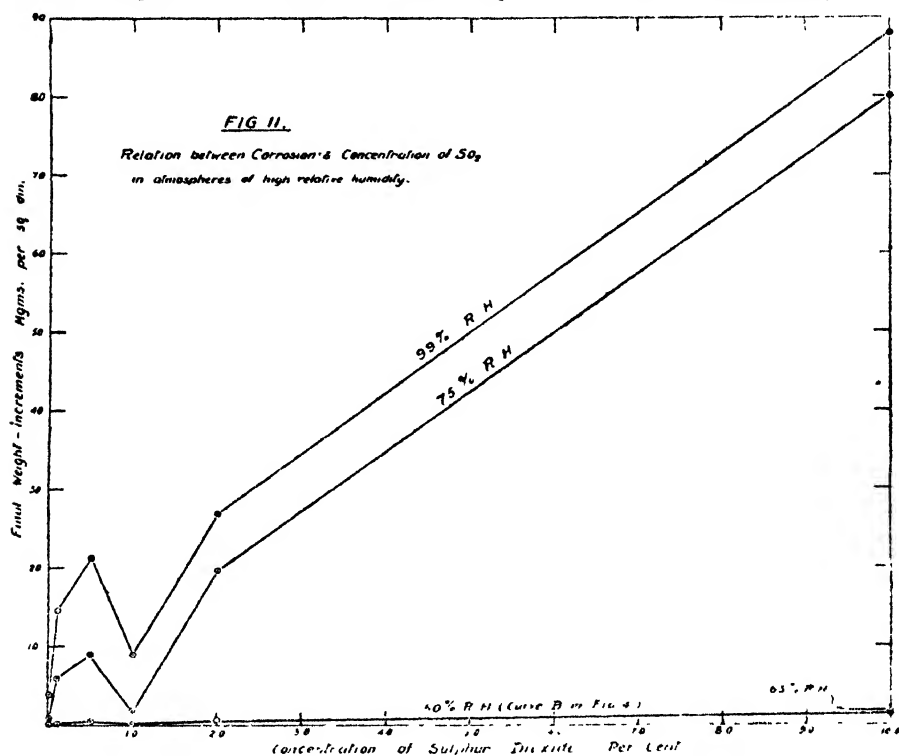
corrosion of iron. The principle was carried to a further stage in the Third Report,[13] particularly in connection with the behaviour of specimens exposed in Stevenson screens. The present experiments leave little doubt concerning the importance of critical humidity in the corrosion of copper, whilst the work of Hudson suggests that it may be of even greater importance in the case of other metals.

A second point of interest presented by Fig. 11 is the marked break in the corrosion-concentration curves toward a minimum corrosion value at 1·0 per cent. sulphur dioxide. This break is shown clearly in the curves for the higher relative humidities (75 and 99 per cent. R.H.), the two curves following an approximately parallel course. It is re-

[12] W. H. J. Vernon, *Trans. Faraday Soc.*, **23**, 140, 162, 1927.
[13] J. C. Hudson, *Trans. Faraday Soc.*, **25**, 204, *et seq.*, 1929.

markable, moreover, that the same break also occurs in the curve for 50 per cent. R.H. ; although the scale of Fig. 11 does not permit this to be seen, the effect is brought out clearly on the larger scale of Fig. 4. The experimental data are sufficiently definite ; although the interpretation of the phenomenon is not obvious, the matter is rendered clearer by a consideration of the following analytical results.

A series of experiments was conducted with the object of determining the composition of the reaction products. Atmospheres were employed, each of 99 per cent. relative humidity, containing sulphur dioxide in the following proportions, $0·5$, $1·0$ per cent. (eight specimens exposed in each), $2·0$ per cent., $4·0$ per cent. (four specimens exposed in each). The experiment was continued for 30 days, the atmosphere being replaced at the usual intervals, the specimens, however, being allowed to remain until the end. Immediately on the conclusion of each experiment the specimens were weighed and the product was removed from them by immersion in standard $N/100$ sulphuric acid. The specimens were then dried and reweighed. SO_4'' was estimated as barium sulphate, and copper [14] as the co-ordinate compound of copper and salicylaldoxime $(C_7H_6O_2N)_2Cu$. The precipitate in each case was centrifuged and weighed in the centrifuge tube, all usual precautions being taken. The amount of $[SO_4]''$ in the product was obtained as the difference between the total $[SO_4]''$ determined and that due to the sulphuric acid used for removing the product. The results are given below. (Previous tests had shown the complete absence of sulphite $[SO_3]''$ from the products.)

$0·5$ *per cent. SO₂ Atmosphere.*
   Weight of copper in product $= 35·87$ mg.
   [Loss in weight of specimens $= 35·72$ mg.]
   Weight in SO_4'' in product $= 41·64$ mg.
   Calculated formula of product $= CuSO_4 + 0·32\ Cu(OH)_2$.

$1·0$ *per cent. SO₂ Atmosphere.*
   Weight of copper in product $= 17·31$ mg.
   Loss in weight of specimens $= 17·27$ mg.]
   Weight of SO_4'' in product $= 28·26$ mg.
   Calculated formula of product $= CuSO_4 + 0·07\ H_2SO_4$.

$2·0$ *per cent. SO₂ Atmosphere.*
   Weight of copper in product $= 15·82$ mg.
   [Loss in weight of specimens $= 15·96$ mg.]
   Weight of SO_4'' in product $= 36·37$ mg.
   Calculated formula of product $= CuSO_4 + 0·34\ H_2SO_4$.

$4·0$ *per cent. SO₂ Atmosphere.*
   Weight of copper in product $=\ \ 3·63$ mg.
   (A portion only of the total product was examined.)
   Weight of SO_4'' in product $= 15·73$ mg.
   Calculated formula of product $= CuSO_4 + 0·65\ H_2SO_4$.

The foregoing results appear to be of considerable significance. In the case of atmospheres containing less than $1·0$ per cent. sulphur dioxide, copper sulphate in the product is associated with excess of base ; atmospheres containing more than $1·0$ per cent. sulphur dioxide, on the other hand, yield products associated with excess of sulphuric acid. The product from

[14] Ephraim, *Ber.*, **63**, [B], 1928, 1930.

the atmosphere containing 1·0 per cent. sulphur dioxide shows fairly close agreement with the composition of normal copper sulphate. The slight excess of sulphuric is very probably due to the critical concentration of sulphur dioxide occurring at a point not exactly coincident with 1·0 per cent. ; it appears reasonable to assume that at the critical concentration the product would consist entirely of normal copper sulphate.

The further suggestion emerges that in atmospheres containing less than the critical concentration of sulphur dioxide (approximately 1·0 per cent.) oxidation of SO_2 to SO_3 is catalysed at the surface of the specimen by metallic copper, and, in the presence of oxygen, copper sulphate is formed ; in the presence of water vapour copper hydroxide is formed concomitantly to an extent that is dependent upon the concentration of sulphur dioxide. In atmospheres containing more than 1·0 per cent. sulphur dioxide, oxidation of the excess of SO_2 is catalysed with the formation of free sulphuric acid. It seems most probable, therefore, that the characteristic shape of the
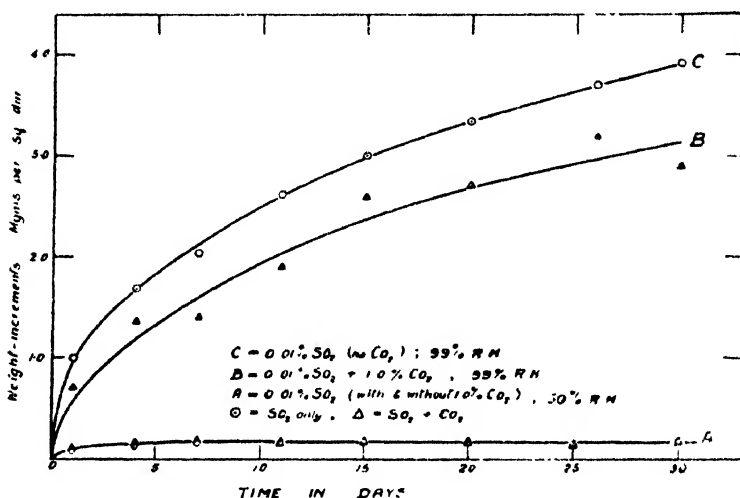
FIG. 12 — Influence of Carbon Dioxide on Corrosivity of Unsaturated
Atmospheres containing Sulphur Dioxide

time-corrosion curves (Fig. 3 and Figs. 5 to 10) is due to the catalytic oxidation of sulphur dioxide, the rate of attack falling off as the active centres on the surface of the specimen become exhausted.

C. Atmospheres Containing Carbon Dioxide (with Sulphur Dioxide).—The influence of carbon dioxide when present in the atmosphere together with sulphur dioxide was investigated by comparing the effects of an atmosphere containing 0·01 per cent. sulphur dioxide with those produced by the same atmosphere to which 1 per cent. carbon dioxide had been added, the experiments being duplicated at relative humidities of 50 per cent. and 99 per cent. The results are shown in Fig. 12. At the lower relative humidity, no difference could be detected in the effects due to the two atmospheres and the two groups of results are plotted in one curve (A). At the higher relative humidity, the atmosphere containing no carbon dioxide gave a rather higher corrosion rate than the atmosphere to which carbon dioxide had been added ; the restraining influence of carbon dioxide appears to be connected essentially with the presence of a very thin film of moisture at the surface.

D. Atmospheres Containing Hydrogen Chloride (with Sulphur Dioxide).—The effect was tried of adding a small amount (0·01 per cent.) of hydrogen chloride gas to an atmosphere containing 1·0 per cent. sulphur dioxide at a relative humidity of 50 per cent. For the first time in the series of experiments, interference colours, in their characteristic order, were developed upon the specimens. The curve is plotted at B in Fig. 13, whilst the straight line at C, derived from squares of points on the main curve, shows this to be a parabola. This is in agreement with previous work (First and Second Reports) in which the development of interference colours was invariably associated with a parabolic curve. The curve for the atmosphere of 1·0 per cent. sulphur dioxide in the absence of hydrogen chloride is plotted at A.

The curve for hydrogen chloride alone is similar to that shown at B, but not so regular. It is probable that sulphur dioxide, in presence of free hydrogen chloride, acts merely as a reducing agent, and serves to maintain the film of reaction product in the cuprous condition. That the
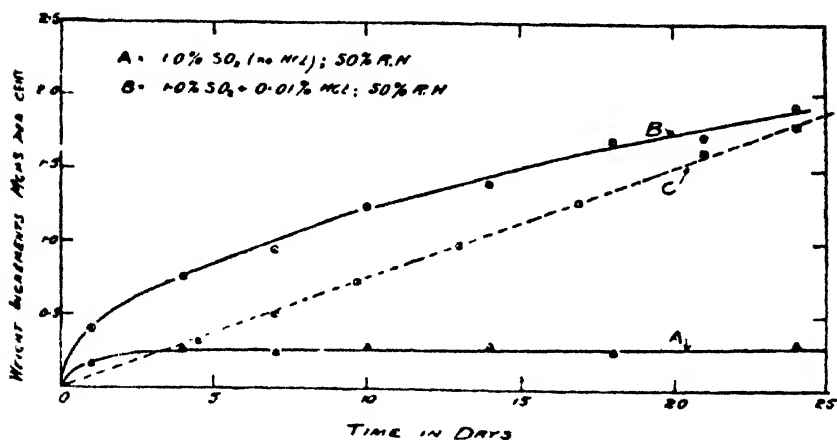
FIG 13 INFLUENCE OF HYDROGEN CHLORIDE ON CORROSIVITY OF UNSATURATED ATMOSPHERE CONTAINING SULPHUR DIOXIDE.

film of product consists of cuprous chloride is confirmed by its photo-chemical properties ; thus, on subsequent exposure to light, an impression of the glass supporting stand was produced upon some of the specimens, corresponding with the shadow thrown by the stand. The foregoing results are of interest as showing that, although sulphur dioxide in the atmosphere normally plays a primary part, in exceptional circumstances it may play a secondary part, depending upon the nature of the added constituent.

2. Saturated and Supersaturated Atmospheres.

In the following experiments, for the purpose of obtaining conditions of complete saturation which would be maintained indefinitely, the modified form of Hempel desiccator shown in Fig. 2 was employed. The specimens were supported on stands similar to those already described (Fig. 1) except that they were smaller, and in some cases carried four specimens only. The cleaned and weighed specimens having been introduced, the vessel was evacuated and refilled with purified air.

Before atmospheric pressure was reached, either distilled water (conductivity water [15] was used in some experiments) or a solution of sulphur dioxide of appropriate concentration was introduced through the stopcock into the annular reservoir. The vessel was either kept in the thermostat at 25° or was allowed to remain on the laboratory bench (protected from direct sunlight) according to the particular experiment.

A. Atmospheres Containing no Added Impurity.—A " blank " experiment was conducted (in thermostat) in which H.C. copper specimens were exposed in the corrosion vessel with conductivity water in the annular reservoir. A definite film of moisture was observed upon the specimens within a few days which persisted throughout the period of exposure. Nevertheless, only a very slight general darkening of the specimens was observed, to appreciate which, comparison with a freshly-cleaned surface was necessary. Weight-increments at seventy-eight and 140 days' exposure respectively were 0·215 and 0·325 mgm. per sq. dm. In a similar experiment at ordinary room temperature, employing specimens of both H.C. and arsenical copper, a greater darkening of the arsenical copper was observed after only one day's exposure.

B. Atmospheres Containing Sulphur Dioxide.—In the following experiments, a saturated solution of sulphur dioxide has been contained in the annular reservoir. The much greater rate of attack (due to the high concentration of sulphur dioxide) as compared with the experiments in Section I, has permitted relatively large amounts of corrosion product to be removed for examination ; the justification for this procedure will appear below.

Visual and Analytical Results.—Within several days the specimens become covered with a film of moisture which collects in drops of pale green liquid at the lower edge. On the upper parts of the specimen very fine crystals (apparently of normal copper sulphate) gradually appear, particularly round the suspension hole, where definite crystals have been observed within three days. In about a week, at which stage the specimens deliquesce freely, the whole surface is covered with a finely crystalline film. The foregoing description applies fairly generally both to H.C. and arsenical copper, except that arsenical copper is characterised by a very rapid darkening in the early stages,[16] resulting in about three days in a nearly black background on which the crystalline film develops.

In an experiment in which four specimens of H.C. copper were contained in the corrosion vessel (the experiment was conducted during the month of July, with the vessel on the laboratory bench, screened from direct sunlight), at the end of twenty-eight days the specimens were covered with a pale blue deposit, whilst 23 c.c. of green liquid had collected at the bottom of the vessel. The specimens were dried *in vacuo ;* the film was removed and analysed with the following result. Copper, 36·5 per cent. (Cu in $CuSO_4$ = 39·6 per cent.) ; sulphate [SO_4], 50·5 per cent. ; sulphite, nil. The green liquid, after boiling with 2N hydrochloric acid with simultaneous passage of a stream of nitrogen to remove any SO_2, was found to contain [SO_4] 0·2005 gram ; Cu 0·0760 gram. This represents an excess of [SO_4] over that required for normal copper sulphate

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[15] Prepared by a routine method in the Corrosion Section of the Chemical Research Laboratory (see Bengough, Stuart and Lee, *J. Chem. Soc.*, **129**, 2156, 1927 ; Stuart and Wormwell, *ibid.*, **132**, 85, 1930)

[16] This confirms earlier observations in connection with the open-air tests at South Kensington (First Report, Vernon, *loc. cit.*, p. 875).

of 0·0855 gram, showing the presence of free sulphuric acid. This result confirms the observation already made that, at the higher concentrations of SO_2, oxidation of sulphur dioxide to sulphuric acid is catalysed at the surface of the specimen independently of the formation of copper sulphate.

Gravimetric Results.—An experiment with H.C. and arsenical copper two specimens of each, exposed in the corrosion vessel with saturated sulphur dioxide solutions, was conducted in the thermostat for twenty days. Weight-increments of the specimens were determined after vacuum desiccation over concentrated sulphuric acid for one week ; the products were then completely removed and the loss in weight of the specimens was determined. The results were as follows :—

Weight-increments (grams per sq. dm.).			*Weight-losses (grams per sq. dm.).*		
H.C. copper.	(1) 0·62414	0·64300	H.C. copper.	(1) 0·21504	0·22612
	(2) 0·66184			(2) 0·23722	
Arsenical copper.	(1) 0·53862	0·51456	Arsenical copper.	(1) 0·19720	0·19734
	(2) 0·49050			(2) 0·17748	

Further experiments were conducted in which specimens of H.C. and arsenical copper were exposed to the saturated atmosphere, both at 25° and at room temperature, for periods of fifty-one and forty-nine days respectively ; four specimens of each material were exposed in each case. The specimens were removed at intervals ; the figures given below are those yielded by the specimen last to be removed ; intermediate values, however, showed approximately the same ratio between H.C. and arsenical copper.

Thermostat 51 days.	Temperature 25°.		
Weight-increments.	H.C. copper.	0·7464 gram per sq. dm.	
	Arsenical copper.	0·5912	,, ,,
Weight-losses.	H.C. copper.	0·3070	,, ,,
	Arsenical copper	0·2188	,, ,,

Room. 49 days	Temperature range 10-23°.	Mean Temperature 16°.	
Weight-increments	H.C. copper.	1·1914 grams per sq. dm.	
	Arsenical copper.	1·4302	,, ,,
Weight-losses.	H.C. copper	0·94058	,, ,,
	Arsenical copper.	0·7156	,, ,,

In the foregoing examples, arsenical copper, with one exception, has yielded a lower weight-increment than has H.C. copper, and in all cases it has yielded an appreciably lower loss in weight. (In experiments of this type, greater significance attaches to loss in weight figures than to weight-increments, owing to the large amount of loosely-adhering product.) These results confirm the results of field tests in the Second and Third Reports,[17] in which the greater resistance of arsenical copper to atmospheric corrosion was shown.

Behaviour of Corrosion Products.—The corrosion products were removed from the specimens by careful scraping with a horn spatula, supplemented occasionally with a nickel spatula. In no case was there any evidence of appreciable pitting of the metal. Underneath the layer of corrosion product, and adhering firmly to the metal, there was a red film, presumably of cuprous oxide, on the H.C. specimens, and a dark brown film on the arsenical specimens. This, again, confirms earlier observations in connection with the open-air tests.[18]

[17] Second Report (Vernon, *loc. cit.*), p. 178 ; Third Report (Hudson, *loc. cit.*), p. 288.
[18] Second Report (Vernon, *loc cit.*), p. 177.

The products from the second series of experiments ("thermostat" and "room") were carefully collected and divided into four groups as follows :—

    (1) "Thermostat Experiment."
            Products from   8 days and 21 days' exposure (mixed).
    (2) "Thermostat Experiment."
            Products from 36   ,, ,, 51   ,,   ,,   ,,
    (3) "Room Experiment."
            Products from   7   ,, ,, 14   ,,   ,,   ,,
    (4) "Room Experiment."
            Products from 27   ,, ,, 49   ,,   ,,   ,,

In each group the products from the H.C. and arsenical specimens were kept separate, so that altogether there were eight separate collections of products. Each of these was placed in a weighing bottle and submitted to vacuum desiccation over concentrated sulphuric acid, in a Hempel desiccator at 25°, with occasional shaking of the product and periodical weighing. The desiccation was continued (the vacuum being maintained by frequent re-evacuation of the desiccator) until approximate constancy of weight was obtained, for which a period of five months was required. (The tenacity with which associated moisture is retained by atmospheric corrosion products from actual field tests, even at a temperature of 100°, has been discussed in a previous paper,[19] in which a characteristic curve was reproduced). A portion of each product was then transferred to a clean dry weighing bottle in sufficient quantity (from 0·2 to 0·3 gram) just to cover the bottom of the bottle. The

FIG 14 — Hygroscopicity of Corrosion Products.
Weight-increments of (previously desiccated, products in atmosphere of 100 per cent relative humidity.

bottles were then placed (the stoppers being removed during the actual experiment) in a large flat-bottomed "crystallising basin" in which they were ranged round a similar, smaller vessel, placed in the middle. The whole was then placed within a bell-jar similar to those used in the main experiments, except that a delivery tube with stopcock passed through the stopper and terminated just above the middle dish. The bell-jar

[19] Vernon and Whitby, *J. Soc. Chem. Ind.*, **47**, 255T (1928).

was placed in the thermostat and, after evacuation, was filled with an atmosphere of 50 per cent. relative humidity by the method already described ; just before the filling was completed, a solution of sulphuric acid (sp. gr. 1·329) was run into the middle dish by means of the delivery tube ; the vapour pressure of this solution was such as would maintain a relative humidity of 50 per cent. and hence compensate for water vapour removed by the desiccated products. After two hours' exposure of the products the bottles were removed for weighing. Subsequently they were replaced, and the experiment was repeated for further periods, the weight of the products being determined after two, six, twelve and twenty-eight hours' exposure. The whole experiment was repeated, with a further batch of dry products, employing an atmosphere of 75 per cent. relative humidity (with sulphuric acid solution of sp. gr. 1·22) ; and again repeated with a final batch of products exposed to an atmosphere of 100 per cent. relative humidity, with distilled water in the middle dish. Typical curves, showing the rate of absorption of water vapour by the desiccated products in an atmosphere of 100 per cent. relative humidity, are given in Fig. 14, where the percentage weight-increments of products from H.C. and arsenical copper are plotted against time. The curves represent the behaviour of products from the first period of corrosion (groups 1 and 3) and the lower curves the be-

FIG 15 CRITICAL HUMIDITY, AS SHOWN BY HYGROSCOPICITY OF CORROSION PRODUCTS (CURVES A & B) AND BY THE CORROSION OF THE METAL (CURVE C) AT A SERIES OF RELATIVE HUMIDITIES

haviour of those from the second period (groups 2 and 4). The results from the "thermostat" and "room" experiments are thus taken together and mean values plotted ; the curves yielded by individual experiments, however, are closely similar. In each case, the product from H.C. copper shows an appreciably greater hygroscopicity than that from arsenical copper ; furthermore, the difference is more marked in the products representing the longer period of corrosion.

In Fig. 15 (curves A and B) the "final" weight-increments (after twenty-eight hours' exposure at each relative humidity) yielded by the

products from H.C. and arsenical copper, are plotted against relative humidity. (This method is similar to that employed by Hudson [20] in the case of corrosion products collected from various specimens in his field tests, except that his products were not subjected to a previous desiccation.) For the purpose of comparison, results obtained in Section I with an atmosphere containing 10 per cent. sulphur dioxide (the highest concentration there employed) are replotted on the same diagram (curve C) ; the values in this case represent the final weight-increments undergone *by the metal* at each relative humidity (including, in this case, an atmosphere of 63 per cent. R.H.), the very great step between 63 per cent. and 75 per cent. relative humidity representing the " critical humidity " which has already been discussed. It is note-worthy that the curves from the present experiments exhibit quite definite breaks in approximately the same position ; the magnitude of these breaks is not so great as that in curve C ; nevertheless, there can be little doubt that they are again determined by the critical humidity, the value for which coincides with that in the previous experiments. It is significant, moreover, that the influence of critical humidity, as shown by curves A and B is more marked in the case of high-conductivity than in the case of arsenical copper.

Reference has already been made to the greater resistance to atmospheric corrosion exhibited by arsenical copper, as compared with high conductivity copper, as shown by exposure tests in the field. Samples of old copper roofings, quite sound after upwards of 100 years' exposure, have been found [21] to be definitely arsenical. In the Second Report it was suggested that the superiority of arsenical copper is due to the presence of a protective film, the development of which in the early stages of exposure to the open-air, had actually been followed by reflectivity measurements. A supplementary factor is now, revealed by the present experiments in respect to the greater hygroscopicity of the product from H.C. copper, and the greater susceptibility of the purer material to changes taking place at the critical humidity. The experiments also suggest that the influence of arsenic is likely to become more marked with increasing period of exposure. This is confirmed by the observation, first made by Hudson,[22] that arsenic actually accumulates in the product during corrosion in the field thus, Hudson found that after a year's exposure (at Birmingham) the ratio of arsenic to copper was four times greater in the product than in the metal.

C. Atmospheres Containing Carbon Dioxide (with Sulphur Dioxide).—In order to ascertain the influence of carbon dioxide, three parallel experiments were carried out in the thermostat with the Hempel desiccator apparatus, as follows : (1) The liquid in the reservoir consisted of one volume of a saturated solution of sulphur dioxide, mixed with 400 volumes of distilled water, yielding a solution having only a " faint smell " of sulphur dioxide ; the vessel was previously evacuated and filled with purified air in the usual way. (2) The reservoir contained one volume of saturated solution of sulphur dioxide, mixed with 400 volumes of saturated solution of carbon dioxide. In addition, 1·0 per cent. carbon dioxide was added to the atmosphere, so that a large excess of carbon dioxide over sulphur dioxide was ensured. (3) The

[20] Third Report (*loc. cit.*), p. 207.
[21] Vernon and Whitby, *J. Inst. Metals*, 42, 189, 202, 1929.
[22] Third Report (*loc. cit.*), p. 237. See also Vernon and Whitby, *J. Inst. Metals*, 42, 202, 1929.

reservoir liquid consisted entirely of a saturated solution of carbon dioxide, whilst 1·0 per cent. carbon dioxide was added to the atmosphere as in (2). In each experiment, four specimens of H.C. copper were exposed to the atmosphere on the usual type of stand, and at intervals up to 320 days, a specimen was removed and its weight-increment determined. The results from experiments (1) and (2) showed an agreement that is somewhat remarkable, as will be seen from Fig. 16, the two series of values lying closely on a single curve. In contrast with
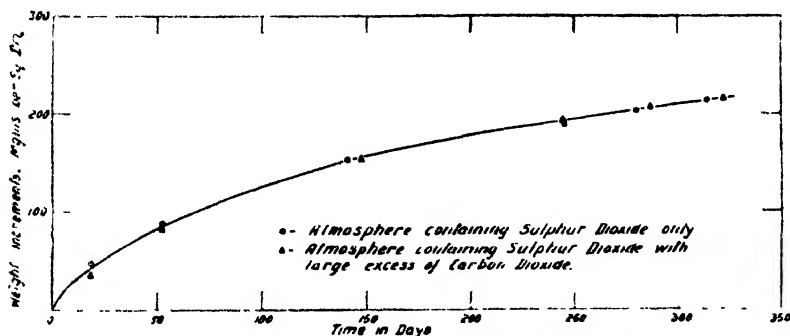
FIG. 16 INFLUENCE OF CARBON DIOXIDE ON CORROSIVITY OF SATURATED ATMOSPHERE CONTAINING SULPHUR DIOXIDE.

the relatively thick, dark green coating produced on the specimens in these experiments, the specimens from experiment (3) had suffered no change in appearance beyond the slight general darkening that is characteristic of exposure in pure saturated atmospheres ; the weight-increment at 245 days was 0·77 mg. per sq. dm. a value too small to be shown on the vertical scale of Fig. 16 (compare 192·4 and 191·9 mg. per sq. dm. in the other experiments). It is evident that the influence of carbon dioxide, in relation to the influence of very much lower concentrations of sulphur dioxide, is quite negligible.

Appendix.

Influence of Surface Condition upon Rate of Attack.

Experiments have been carried out in which, instead of the usual treatment with fine emery paper (see p. 257), specimens have been prepared by the method of sand-blasting.[23] White Calais sand was employed for this purpose and was ejected from the nozzle (7/16″ diam.) at a pressure of 7 lbs./sq. inch, the specimens being held at a distance of approximately 12 ins. from the nozzle. The specimens were exposed to an atmosphere containing 1·0 per cent. sulphur dioxide at a relative humidity of 99 per cent. The results are plotted in Fig. 17 (Curve B) together with (Curve A) the results yielded by specimens prepared with fine emery paper (see also curve C in Fig. 8). It will be seen that the sand-blasted specimens have undergone a profoundly greater attack as compared with the emeried specimens. Nevertheless, satisfactory reproducibility is yielded, as shown by the duplicate figures in Table I. (these are given for a period of 11 days only). The weight-increments yielded by duplicate experiments with emeried specimens, for a similar period, are also included.

[23] Through the kind offices of Mr. C. R. Clark, Central Technical College, Birmingham.

TABLE I.—ATMOSPHERE CONTAINING 1·0 PER CENT. SO$_2$; 99 PER CENT.
RELATIVE HUMIDITY.

Surface Condition of Specimen.	Expt.	Time in Days, with Weight-Increment in Mgs. (Actual).[24]			
		1.	4.	7.	11.
Sand-blasted	A	26·3	39·9	43·5	46·6
,,	B	25·9	38·8	43·6	47·2
Emeried	A[25]	2·42	2·85	2·70	3·27
,,	B[25]	2·38	2·73	2·88	3·37

The experiment described above was repeated with an atmosphere containing 1·0 per cent. sulphur dioxide as before, but having a relative humidity of only 50 per cent. (*i.e.* less than the critical humidity). In this case the disparity between emeried and sand-blasted specimens was not so pronounced, equilibrium values being 0·32 and 1·56 mg. sq. dm. respectively (compare 8·0 and 101·0 mg./sq. dm. for the atmosphere of 99 per cent. relative humidity). This suggests that the effects due to critical humidity, as described in the text, would have been greatly intensified had the experiments been conducted upon sand-blasted specimens.

In order to ascertain the influence of surface under entirely different conditions of

FIG. 17. INFLUENCE OF SURFACE CONDITION OF METAL UPON RATE OF ATTACK.

[24] To convert to mg. per sq. dm. (as plotted), figures should be doubled.
[25] Expt. A was started on 9th January, 1930. Expt. B on 5th February, 1931.

attack, experiments were conducted in an atmosphere containing 0·01 per cent. of hydrogen sulphide at a relative humidity of 50 per cent. Four specimens were employed in each experiment; they were withdrawn from the bell-jar precisely five minntes after the admission of hydrogen sulphide. This period was sufficient to produce a uniform tarnish of purple colour on the emeried specimens; in all cases there was appreciable excess of hydrogen sulphide in the bell-jar when the specimens were withdrawn. The results of duplicate experiments on both emeried and sand-blasted specimens are given in Table II.

TABLE II.—ATMOSPHERE CONTAINING 0·01 PER CENT. H₂S; 50 PER CENT. RELATIVE HUMIDITY.

	Weight-Increments, Mgs. (actual), of Individual Specimens after 5 Minutes' Exposure.	
	Expt. A.	*Expt. B.*
	0·10	0·10
Sand-blasted specimens	0·09	0·09
	0·11	0·09
	0·11	0·11
Mean value . . .	0·10	
	Expt. A.	*Expt. B.*
	0·06	0·06
Emeried specimens	0·06	0·06
	0·06	0·05
	0·07	0·07
Mean value . . .	0·06	

The mean weight-increments are 0·10 and 0·06 mg. respectively. These values are plotted in Fig. 17 on the assumption that the process is controlled by film formation, and, hence, that the characteristic curve is the parabola; this assumption, in the case of tarnish films showing interference colours, is amply justified by the results of previous work.[26] Nevertheless, a consideration of the isolated points alone is sufficient to show that surface condition has a far smaller effect upon the "hydrogen sulphide type" of attack than upon the "sulphur dioxide type."

The foregoing results provide an interesting sequel to those recorded in the text. Thus, it was concluded that in an atmosphere containing sulphur dioxide and moisture, the corrosion process is controlled by the catalytic oxidation of sulphur dioxide at the metal surface, the actual rate of attack depending upon the number of active centres that are available. It can readily be understood that a specimen in the sand-blasted condition will present a greater number of such active centres than a specimen that has been polished with fine emery, to an extent that is quite disproportionate to the increase in total surface area. On the other hand, in the hydrogen sulphide type of attack, where the process is controlled by gaseous diffusion through an initially formed film, the reaction product, from the outset, takes the form of a continuous envelope; hence the magnitude of the attack would be expected to be in simple proportion to the surface area.

[26] See, for example, "First and Second Reports," *loc. cit.*

Summary and Conclusions.

A technique is described for studying the atmospheric corrosion of metals in the laboratory by exposure of specimens to synthetic atmospheres. The corrosion of copper, in air containing sulphur dioxide, at various relative humidities, has been investigated. At zero relative humidity, the action of air containing various concentrations of sulphur dioxide, from 0·01 to 10·0 per cent., is indistinguishable from that of purified air ; no visible effect is produced upon the specimens and the weight-increment is in the neighbourhood of the lowest limit of measurement by the methods employed. The introduction of water vapour brings about an immediate differentiation among the various concentrations of sulphur dioxide. Corrosion-time curves have been plotted for relative humidities of 50, 63, 75 and 99 per cent. The curves are exponential in form in the early stages, and then flatten toward the time axis, with which they become nearly parallel in from thirty to forty days. The process is controlled by the catalytic oxidation of sulphur dioxide at the metal surface, the rate of attack falling off as the active centres are used up. At 50 per cent. relative humidity the relationship of the atmospheres among themselves in respect to their action upon copper is similar to that which obtains at the higher relative humidities, but the magnitude of the attack is of a definitely lower order. Between 63 per cent. and 75 per cent. relative humidity there is, in most cases, a profound increase in the rate of attack, pointing to the existence of a critical humidity lying between these values. The curves connecting rate of corrosion with concentration of sulphur dioxide show, in all cases, a break toward a minimum value at approximately 1·0 per cent. sulphur dioxide. In atmospheres of this critical concentration, the reaction product consists of normal copper sulphate ; at lower concentrations of sulphur dioxide it is accompanied by excess of base, and at higher concentrations by excess of sulphuric acid. Carbon dioxide, when present in large excess over sulphur dioxide, is without appreciable influence. Hydrogen chloride, on the other hand, when present in considerably lower concentration than sulphur dioxide, pursues an independent and (in atmospheres of relatively low humidity) much greater attack upon the metal ; the attack, however, is of a different type, being represented by a parabolic corrosion-time curve (similarly for copper in atmospheres containing hydrogen sulphide), and consisting in the production of a series of interference colours due to a film of cuprous chloride. The surface condition of the metal has a pronounced effect upon the first type of attack (controlled by catalytic oxidation of sulphur dioxide), but a comparatively small effect upon the second type (controlled by gaseous diffusion through a continuous envelope of reaction product).

Experiments have also been carried out with saturated and supersaturated atmospheres containing sulphur dioxide. A greater rate of attack has been observed upon high conductivity than upon arsenical copper, confirming the results of earlier field tests, and the development of a dark film upon the arsenical copper in the initial stages has also been confirmed. The hygroscopicity of the corrosion products, after prolonged desiccation, has been studied at relative humidities of 50, 75, and 100 per cent. ; there is a marked increase between 50 and 75 per cent. relative humidity, corresponding with the critical humidity previously observed. The influence of critical humidity is more marked upon the products from H.C. copper than upon those from arsenical copper ; the products from H.C. copper, moreover, are definitely more hygroscopic than those from arsenical copper. This provides an additional explanation for the greater corrosion resistance of arsenical copper as observed in open-air exposure.

THE RELATION OF THE MOISTURE IN RUST TO THE CRITICAL CORROSION HUMIDITY.

By W. S. Patterson and L. Hebbs.

A very extensive literature exists dealing with the corrosion of iron and steel ; and during the last decade the study of the subject has been considerably modified and advanced by the new theories of the chemistry of corrosion which have been propounded by Evans and Vernon.[1]

No feature of this newer aspect of corrosion theory has been more fundamental than the appreciation of the importance of the effects, both physical and chemical, of the corrosion products.   These substances, which are almost invariably produced by the interaction of the anodic and cathodic products, and which are therefore secondary products, in a large measure determine the character and distribution of subsequent corrosion.

The importance of rust, the corrosion product of iron, in increasing corrosion speed has recently been demonstrated by Vernon [2] working with unsaturated atmospheres, and also by one of the present authors,[3] who has shown that rust accelerates corrosion of the metal when exposed in a saturated atmosphere.   Vernon further made the important observation that there is a critical humidity which must be exceeded before this rapid acceleration in corrosion speed will occur.   His experiments and the very convincing graph published indicate that for his samples a critical value somewhere between 43 per cent. and 68 per cent. relative humidity had to be exceeded.   An explanation of this phenomenon must be an essential factor in any theory of the atmospheric corrosion of iron.   Hudson [4] has therefore examined rust by exposing it to conditions of increasing humidity in order to ascertain if an abnormal change in deliquescence was exhibited as some critical humidity.   The failure to obtain evidence of this anticipated change has been attributed by Vernon [5] to the fact that the rust specimens used by Hudson had already passed through the critical humidity before the experiments, and had therefore previously received the weight increments which it was hoped to measure during the experiments.

The authors consider it unnecessary to assume that rust is abnormally deliquescent at, and above, the critical humidity corresponding

[1] " Corrosion of Metals," U. R. Evans (E. Arnold) ; Trans. Faraday Soc., 19, 1924 ; 23, 1927.
[2] Ibid., 23, 162, 1927.   [3] J.S.C.I., 49, 204 T., 1930.
[4] Trans. Faraday Soc., 25, 240, 1929.
[5] Discussion on Hudson's Paper (4).

to rapid increase in corrosion, and have confirmed that no large weight increment does, in fact, occur in the humidity range indicated.

Further, rust will still hold from 50 to 20 per cent. of water, even after lengthy exposure to 0 per cent. humidity conditions, and only takes up an additional 5 to 7 per cent. of water when taken through a whole range of atmospheres of from 0 to 100 per cent. humidity. This suggests that it is the condition rather than the amount of the water present which is an important factor in the promotion of corrosion by rust. The relatively small additional amount of water taken up at, and above, the critical humidity does not appear to be a sufficient explanation for the very large increase observed in speed of corrosion when rust coated metal is maintained above the critical humidity.

Assuming that rust has a gel structure, the authors consider that the work here reported can be interpreted as showing a correlation between these apparently anomalous factors. It might then be possible for a relatively small increase in water content immediately above the critical humidity to render available for the furtherance of corrosion the much larger amount of water already present in the gel, but previously held in constraint by the gel at humidities below the critical value.

The rust samples used were obtained from mild steel (0·18 per cent. carbon). The metal was exposed in the form of plates which were attached to wooden frames by mild steel wire. The rust produced was removed from the plates with a blunt tool. The following are the details, of the exposures of the various samples :—

Rust I.—From exposure for two months, outdoor, Clerkenwell, London.
Rust II.—From exposure for three months in atmosphere of indoor swimming bath.
Rust III.—As I.
Rust IV.—As I., but from prolonged exposure.
Rust V.—As II., but from prolonged exposure.

The amounts of rust obtained in this manner and used in the subsequent experiments ranged from 0·68 to 0·97 grams. Weighing bottles of about 15 c.c. capacity were used, and the rust spread as a thin layer on the bottom of each bottle. These were then placed in an ordinary glass " dessicator " which contained sulphuric acid of the concentration necessary to give the required humidity, and the whole immersed in water as deeply as was safely possible in a thermostat at 20° C. The lid was not at the same temperature as the rest of the apparatus, and to avoid the possibility of condensed water dropping into the weighing bottles when working with high humidities a V-shaped cover was placed between the lid and the bottles. The results obtained were to some slight extent effected by temperature changes of the room during the work, presumably because of the relatively large area of the lid exposed to the atmosphere of the room and not directly in contact with the water of the thermostat. This effect was, however, considerably mitigated by the V-shaped cover mentioned above, which also served to form an insulating layer between the lid above and the bottles below. The extent of variation produced is shown in Table I., which gives the results obtained with two samples of rust and one of china clay when all three were simultaneously exposed to saturated conditions. The sample of china clay was used throughout as a " blank " or independent check, which was not likely to be chemically reactive.

It will be observed that the fluctuations in weight found in the three samples definitely follow parallel curves, and must therefore be related to an outside source.

The amounts gained in weight reported as per cent. in this and other tables have been calculated on the weights obtained when the respective samples were exposed over concentrated sulphuric acid.

A sample of outdoor rust (Rust I.) was exposed to atmospheres of gradually increasing humidity (forty-eight hours at each stage) with the results shown in Table II. and Fig. 1. The sample could not be re-dried to within 0·9 per cent. of its " dry " weight (*i.e.* its weight at 0 per cent. humidity) during twelve hours in a water oven at 90-100° C. Following this, however, ten hours in an air oven at 105° C. reduced the weight to 0·1 per cent. below the original " dry " weight. The sample was now exposed to saturated conditions for twenty days, and although the weight remained almost constant from the first weighing, at the end of one week, the total increase in weight amounted to only 4·98 per cent. as compared with the 6·76 per cent. increase shown by the sample prior to heat treatment. The sample was now exposed to atmospheres of decreasing humidity (ninety-six hours at each stage) with the results shown in Table II.

A sample of rust obtained from the plates exposed in the atmosphere of the swimming bath (Rust II.) was dried in an air oven to constant weight, and exposed firstly to successive stages of progressively increasing hu-

------ Rust I   FIG. 1.
———— Rust II

midity and then to stages of decreasing humidity. The results obtained are given in Table III. and graphically in Fig. 1. The sample was kept at each stage for four or more days. The type of curve obtained, and the lowering of capacity for water which results from drying at 105° C., appeared to indicate that in attempting to ascertain the moisture conditions in rust which correspond with critical corrosion humidity conditions, it was desirable that rust should be used just as scraped from the metal, and should be exposed firstly to saturated and then progressively decreasing humidity conditions.

The results obtained in this manner with two " Outdoor " rusts and one " Swimming bath " rust are given in tables Nos. V., VI., and, VII. Included in these tables are details of the time taken at each stage, the average loss in weight, and the amount of variation observed during the period between the time when equilibrium appeared to have been obtained and when the final weighing was taken prior to altering the humidity conditions. This point is made clear by Table IV., which gives the actual weight variations observed with a sample of " Outdoor rust," when exposed to 25 per cent. humidity conditions.

In the example given in Table IV. equilibrium appeared to have been reached at 120 hours, and the weights obtained between 120 and 288
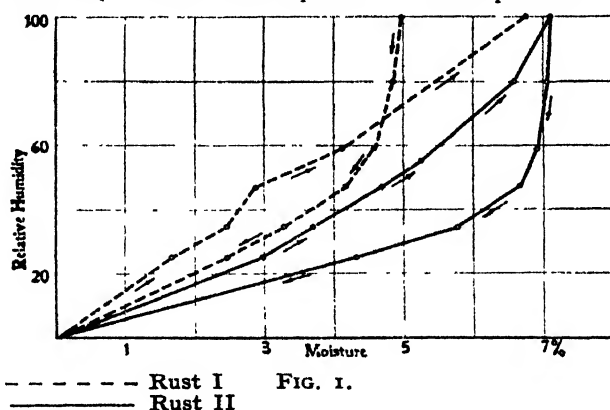
TABLE I.—WEIGHT CHANGES AT CONSTANT HUMIDITY.

Hours Exposed.	Outdoor Rust. Total Gain Weight (mgm.).	Swimming Bath Rust. Total Gain Weight (mgm.).	China Clay. Total Gain Weight (mgm.).
54	24·4	57·5	12·9
84	24·0	57·0	10·9
108	24·4	57·7	11·9
132	25·4	60·0	14·5
156	24·4	58·5	12·5
175	23·4	56·5	10·0
226	24·6	59·3	13·5
245	24·2	58·1	11·5

TABLE II.—RUST I. : WEIGHT CHANGES WITH INCREASING AND DECREASING HUMIDITY.

	Nil	25	35	47	59	80	100
Humidity per cent.　.　.　.	Nil	25	35	47	59	80	100
Total increase in weight (mgm.)　.	—	16	24	28	40	—	66
Total increase in weight per cent.　.	—	1·64	2·46	2·87	4·10	—	6·76
Amount of removable moisture retained per cent. (decr. humidity) .	0	2·46	3·28	4·17	4·56	4·82	4·98

TABLE III.—RUST II. (SWIMMING BATH) : WEIGHT CHANGES WITH INCREASING AND DECREASING HUMIDITIES.

Humidity per cent.　.　.　.	Nil	25	35	47	55	80	100
Total increase in weight per cent.　.	0	2·97	3·69	4·71	5·23	6·58	7·07
Humidity per cent.　.　.　.	100	80	59	47	35	25	0
Amount of removal moisture retained per cent..　.　.	7·07	7·04	6·90	6·63	5·74	4·30	0

TABLE IV.—OUTDOOR RUST.　WEIGHT CHANGES AT 25 PER CENT. HUMIDITY.

Time (hrs.).	Weight (mgm.).	Time (hrs.).	Weight (mgm.).
24	702·5	192	698·5
48	699·9	214	698·5
67	699·1	235	698·5
120	698·0	264	698·3
144	698·0	288	698·3
168	698·3		

TABLE V.—RESULTS OBTAINED WITH OUTDOOR RUST (FROM SHORT EXPOSURE)

(*Rust III.—Using 683·5 Mgm. Weight at Nil Humidity.*)

	100	80	55	38	25	0
Humidities per cent.　.　.　.	100	80	55	38	25	0
Time to equilibrium (hours)　.　.	389	102	167	52	120	313
Total time (hours)　.　.	431	244	239	355	288	408
Average loss in weight (mgm.)　.	—	2·8	4·9	2·1	7·2	14·8
Max. variation (mgm.) Plus　.	0·1	0·4	0·1	0·4	0·2	0·4
,,　　,,　Minus .　.	0·2	0·4	0·1	0·4	0·3	0·3

TABLE VI.—Results Obtained with Outdoor Rust (from Long Exposure.)

(Rust IV.—Using 643·4 Mgm. Weight at Nil Humidity.)

Humidities per cent.	100	82	55	38	25	0
Time to equilibrium (hours) . . .	244	102	141	162	120	313
Total time (hours)	286	244	239	355	288	408
Average loss in weight (mgm.) . .	—	1·7	3·4	1·9	6·2	9·4
Max. variation (mgm.) Plus . . .	0·2	0·5	0·9	0·6	0·4	0·7
,, ,, Minus . . .	0·1	0·1	0·3	0·4	0·1	0·2

TABLE VII.—Results Obtained with Swimming Bath Rust.

(Rust V.—Using 961·5 Mgm. Weight at Nil Humidity.)

Humidities per cent.	100	80	55	38	25	0
Time to equilibrium (hours) . . .	365	78	141	96	144	361
Total time (hours)	431	244	239	355	288	408
Average loss in weight (mgm.) . .	—	2·6	8·8	3·9	20·5	31·2
Max. variation (mgm.) Plus . . .	0·1	0·6	0·4	0·5	0·6	0·6
,, ,, Minus . . .	0·1	0·4	0·6	0·5	0·2	0·2

TABLE VIII.—Analysis. Calculated as Per Cent. on Weight at Nil Humidity.

	Loss on Ignition.	Fe_2O_3.	Cl_2.
	Per Cent.	*Per Cent.*	
Rust No. III.—Outdoor .	19·21	81·41	—
Rust No. IV.—Outdoor .	15·01	85·37	—
Rust No. V.—Swimming Bath	17·91	82·33	0·47

TABLE IX.—Results Obtained with Decreasing Humidities.

(Total Water Present as Mols. of H_2O per mol. Fe_2O_3.)

Humidity. Per Cent.	Rust III.	Rust IV.	Rust V.
100	2·54	1·89	2·61
80	2·49	1·86	2·58
55	2·42	1·81	2·48
38	2·38	1·78	2·44
25	2·27	1·68	2·21
0	2·03	1·53	1·86

hours were averaged, giving a value of 698·3 mgm., with a variation of plus 0·2 and minus 0·3 mgm.

The samples reported in Tables V., VI., and VII. (Rusts Nos. III., IV., and V.) were then examined in the following manner. A weighed portion of the sample was heated to a dull red heat in a platinum dish until no further loss in weight was observed, heating for half an hour being always sufficient for this purpose. Further portions were dissolved in nitric acid and used for the estimation of iron and, when present, chlorine. The results obtained are given in Table VIII.

Since the value for loss on ignition may include loss in weight due to some Fe_2O_3 going to Fe_3O_4, the amounts of water present are best obtained by difference by subtracting the percentage Fe_2O_3 (and Cl_2) content from 100 per cent.

Using the values thus obtained in conjunction with the results given in Tables V., VI., and VII., the changes in total moisture content with changes in humidity were calculated in terms of molecules of water per molecule of ferric oxide, and are given in Table IX., and also in Fig. 2.

The type of curve obtained and the marked hysteresis between values obtained with increasing and decreasing humidity conditions (as shown in Fig. 1) indicate that iron rust has a gel structure. The results here obtained for rust are almost identical with those obtained with precipitated iron hydroxide by van Bemmelen.[6] This is only what might be expected from the known properties of iron hydroxide, which has been formed by precipitation, and from the fact that rust is itself a precipitated product. Starting with this assumption, the results above recorded can be interpreted in the following manner, which is an application of Zeigmondy's[7] theory of gel structure, as worked out for silicic acid, and which is based on Lord Kelvin's[8] calculation of vapour pressure in capillaries.
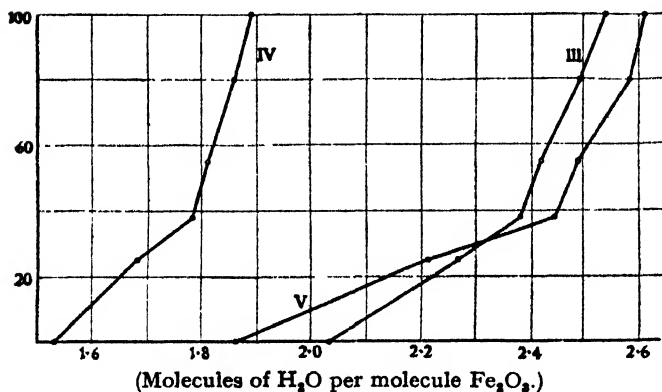
(Molecules of H_2O per molecule Fe_2O_3.)

FIG. 2.

Consider the graphs obtained when working with progressively decreasing humidities. In dropping from 100 per cent. to 40 per cent. saturation a relatively small amount of moisture is lost by the rust. During this process the exterior surface of the water in the capillaries of the gel has changed from the plane surface, which was in equilibrium with the saturated atmosphere, through successive stages of increasing curvature. At about 40 per cent. saturation the smallest possible value has been reached for the radius of curvature, of the surface of the water in the capillary, consistent with the diameter of the capillary here obtaining.

Therefore, when exposed to less than 40 per cent. saturation conditions water is given up to the atmosphere in relatively larger quantities than at the higher vapour pressures, since the minimum vapour pressure for free water in these capillaries has been reached, and hence " free " water can thereafter no longer remain in the rust. The water now remaining is not free water, but water which is strongly adsorbed by the surface of the gel and the walls of the capillaries, and is probably " oriented " by these surfaces. The greater part of this water is apparently so

[6] Z. anorg. Chemie, 20, 185-211, 1899.   [7] Ibid., 71, 356, 1911.
[8] Proc. Roy. Soc., 7, 63-68, 1870.

strongly held that it is not removable even when exposed to concentrated sulphuric acid.

This water must be held by considerable force, and must of course be pressing on the gel with a similar force, so that the rust and the water remaining present when below 40 per cent. saturation are in a state of mutual compression. This water, whether present as adsorbed vapour or liquid, may be assumed to be not free to participate in the furtherance of corrosion. But when the gel is maintained above its " critical humidity," *i.e.* when the external vapour pressure is equal to, or greater than, that vapour pressure given by water, the surface of which has the minimum radius of curvature possible in the capillaries of this gel, then these capillaries commence to fill with water.

The higher the humidity the more nearly does the water surface approach to a plane surface. When the capillaries contain free water, then the gel is no longer under compression, and therefore it must be presumed that the adsorbed water is no longer strongly held. Therefore at the " critical point " there is likely to be only a small increase in moisture content of the rust, but a much larger amount of water (15-20 per cent. on the rust) thus may become available to participate in the furtherance of corrosion. This is in accord with the findings of Vernon,[1] as previously mentioned, who found that rust accelerates the corrosion of iron when in an unsaturated atmosphere. Further, the approximate region of the " critical point " for the first occurrence of " free " water in rust, as here indicated, is in good agreement with the critical point for rapid increase in speed of corrosion of rust covered metal as shown by Vernon's work.

The authors desire to acknowledge their indebtedness to Mr. F. Greenane for his assistance in the laboratory work.

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A NOTE ON THE THERMAL DECOMPOSITION OF POTASSIUM CHLORATE.

By J. B. M. Coppock, J. Colvin, and J. Hume.

Certain experiments on the decomposition of potassium chlorate suggested that microscopic observation of the crystals would be of interest, in view of the results obtained with potassium hydrogen oxalate hemihydrate.[1]

Potassium chlorate twice recrystallised from distilled water, was prepared in the form of thin plates of 1 to 2 mm. length. Suitable crystals of shape as shown in Fig. 1, as free as possible from etched markings, were carefully dried at room temperature. Single crystals were heated at 223 ± 2° C. on the microscope stage and observed by

[1] Hume and Colvin, *Proc. Roy. Soc.*, A, 125, 635, 1929.

transmitted light at intervals of half an hour. For a period of six hours no change was evident. On further heating two rows of dark spots in positions *ab* and *ef* in close proximity and parallel to the edges AB and EF, appeared. These developed until they presented the appearance of continuous broad lines, which progressively increased in breadth. A little later lines of dots parallel to the edges BC, CD and DE, and also lines *a'b'* and *e'f'* parallel to and inside the first lines developed. This proceeded until the whole crystal was covered with regularly arranged lines and dots.

The successive stages are shown in the photographs taken, (1) before heating and (2) after heating for seven hours and (3) after heating for twelve hours respectively. It was found impossible to prolong the observations beyond this period, on account of fracture of the crystals. Kohlschütter and Luthi [2] have observed similar regularly arranged decomposition markings in the incipient dehydration of crystals of hydrated salts.
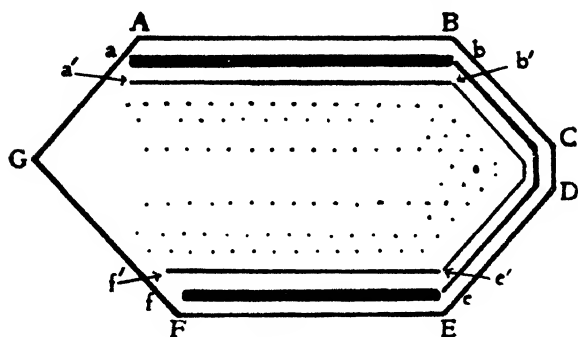
FIG 1.

When the crystals presented the appearance shown in the last photograph, the presence of potassium chloride was established. Similar tests failed to show the presence of chloride in the original crystals.

From these observations it is to be concluded that at 223° the decomposition of potassium chlorate is interfacial and proceeds from nuclei on the surface. In view of this it was thought that the catalytic action of manganese dioxide might be due to increase in the rate of nucleation. Crystals of potassium chlorate in light contact with particles of manganese dioxide and rubbed with manganese dioxide failed to show any increase in the rate of decomposition.

[2] Kohlschütter and Luthi, *Helv. Chim. Act*, **13**, 978, 1930.

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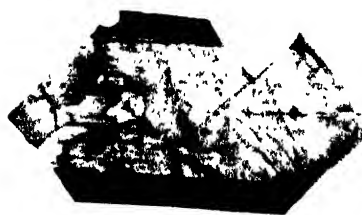
To face page 284.

THE CALCULATION OF THE EQUIVALENT CON-DUCTIVITY OF STRONG ELECTROLYTES AT INFINITE DILUTION.   A REPLY TO SOME RECENT CRITICISM.

By Allan Ferguson and Arthur Israel Vogel.

Some years ago [1] the authors of the present paper discussed the data available for the determination of Λ_0, the limiting value of the equivalent conductivity of a solution as the concentration approaches zero, and, by a graphical method, deduced values for Λ_0 for a large number of electrolytes. These values seemed to the authors to have some advantages over the values heretofore used, and indeed, the primary object of the authors' work has been to provide the most reliable value for this important constant that the experimental data will permit.

The method has been widely discussed, and it would seem that the present time is opportune to sum up and to reply to the criticisms of the method that have been advanced.

It may be useful to give an outline of the method. The experimental figures are plotted on a graph which shows conductivities as ordinates and concentrations as abscissæ. A smooth curve is then drawn through the experimental points using a suitable spline, and from this curve, a series of values of Λ is read off, which correspond to a series of values of the concentration increasing in a known geometrical progression of common ratio r.   If then we assume

$$\Lambda = \Lambda_0 - BC^n \qquad . \qquad . \qquad . \qquad . \quad (1)$$

we have for the next value of Λ,

$$\Lambda + \Delta\Lambda = \Lambda_0 - B(rC)^n \qquad . \qquad . \qquad . \quad (2)$$

leading to

$$\log \Delta\Lambda = n \log C - \log B (1 - r^n) \qquad . \qquad . \quad (3)$$

Hence, if equation (1) represents the relation between Λ and C, a plot of $\log \Delta\Lambda$ against $\log C$ will be rectilinear and will give the values of n and B.   These being known, from every value of Λ and C we can, using equation (1) calculate a value of Λ_0 ; and the mean of these values is taken as the most probable value of Λ_0.

This harmless and elementary procedure—a simple illustration of ordinary methods of accurate graphical work—has, in one aspect, had its importance over-estimated, in another, its accuracy depreciated to an extent which shows that, possibly on account of our own defects of speech, our critics have seriously misinterpreted both our work and our aims.

Thus, we are told that our " method challenges the whole inter-ionic attraction theory " ; that we " reject Kohlrausch's square-root rule " ; that our " results are directly opposed to the theory of Debye and

[1] *Phil. Mag.*, **50,** 971, 1925.

Hückel " ; of the process itself it is remarked that it " as a whole is not reproducible in the hands of different workers," and that " the variations in n are doubtful." Let us review a few of these startling pronouncements a little more closely.

The critics who have discussed our results in detail are Dr. Martin,[2] Professor Newman,[3] and Mr. Davies.[4] Dr. Martin has used the process over a wide range, and finds that equation (1) where n is, on occasion, sensibly different from 0·5, fits the observed results more closely than does the equation of the square-root law. His remarks are eminently constructive and helpful, and this applies particularly to his suggestion that an interpolation curve may be usefully constructed by plotting Λ against log C instead of against C, as is our usual practice. He remarks further (loc. cit.,[2] p. 3285), " exception must be taken to Ferguson and Vogel's practice of testing the fit of their equation by comparing the consistency of Λ_0 calculated from it with that of those calculated from the square root law, using in both cases rounded values of Λ read off from a plot of Λ against C, that is from the curve whose equation is $\Lambda_0 = \Lambda + BC^n$. The consistency of the values of Λ_0 so determined from their equation is a measure, not of its agreement with experiment but of the skill with which a curve of the form $\Lambda_0 = \Lambda + BC^n$ has been drawn and its constants determined. Equation (1) is therefore represented in an unduly favourable light."

This criticism seems to us something of a $\ddot{v}\sigma\tau\epsilon\rho\sigma\nu\ \pi\rho\acute{o}\tau\epsilon\rho\sigma\nu$. The curve between Λ and C, or, for the matter of that, between Λ and log C is drawn primarily for the purpose of graphical interpolation -- a common, everyday operation of the physical and physico-chemical laboratory. A certain amount of skill is necessary in judging the final position of the spline—less in this than in most cases on account of the high accuracy of the observations but this has no more sinister meaning than the skill which attaches to any of the operations employed in measuring a conductivity, whether it be that of washing out the conductivity cell or determining the position of minimum audible sound. This interpolation could be carried out by complex analytical methods which would doubtless pass uncriticised. The results would be indistinguishable from the simple graphical method which we employ. What the equation to the curve will turn out to be is a matter for further consideration—it may, or may not, be represented by $y = a + bx^n$. That is a point which is tested by the process and concerning which we have no preconceptions. But this process, considered as a preliminary step in the proceedings is the ordinary process employed for interpolation, and nothing more. It is, it seems to us, an error to say that we are using the curve $y = a + bx^n$ to test the equation $y = a + bx^n$. A practically identical curve would be obtained by any skilled observer who used the spline, and it is the form of the curve which is the subject under investigation.

We shall return to this point later. Here it is profitable to discuss briefly the extent of interpolation used in obtaining our primary figures as this is germane to Dr. Martin's criticism. Mr. Davies (loc. cit.,[4] p. 82) remarks " Ferguson and Vogel's method of calculation has the disadvantage that the actual experimental figures cannot be used ;

[2] J. Chem. Soc , 3270, 1928 , 530, 1930.
[3] Newman, Electrolytic Conduction, Chapman & Hall, 1930.
[4] Davies, The Conductivity of Solutions, Chapman & Hall, 1930. Compare also Hunter, Ann. Rep. Chem. Soc., 24, 24, 1927.

conductivity values at suitable concentration intervals must first be read off from a ' smoothed ' curve."

In the first place, we deprecate this manner of referring to interpolation processes, as something undesirable and indeed impossible to carry out with exactness. We can assure Mr. Davies that interpolation processes, graphical or analytical, are carried out daily in physical and physico-chemical work, and results deduced from interpolated figures do not suffer by comparison with those deduced from direct experimental figures. Interpolation is by no means an art of recent birth, and we have been on our guard against those elementary errors of drawing concerning which Mr. Davies is so rightly meticulous. But the amount of interpolation employed in calculating the separate values of Λ_0, the mean of which gives our final value is considerably less than is supposed—indeed, is practically negligible. In our original paper,[1] the separate values of Λ_0 are calculated from values of Λ given for the round concentrations of 1, 2, 5, 10, 50, and 100 $\times$ 10^{-4} and it has been assumed that these are values read from the smoothed curves. But it happens that Kohlrausch and his colleagues, from whose experimental figures many of our results are deduced, worked almost exactly at these concentrations [5] and the amount of the interpolation necessary to bring the experimental figures to correspond to these round values of the concentration is of the order of the uncertainty introduced into the experimental figures by temperature variations during the experiment. Table I. shows the amount of the correction involved which is of the order of one or two parts in 10,000.

TABLE I.— POTASSIUM CHLORIDE.[5]

Concentration.	Λ observed.		Correction.
	Series (a)	Series (b)	
0·0001037	129·06	129·03	+ 0·015
0·0002053	128·75	128·76	+ 0·015
0·0005115	128·06	128·08	+ 0·021
0·0010170	127·32	127·30	+ 0·024
0·0020156	126·30	126·28	+ 0·014
0·0050023	124·41	124·37	+ 0·012
0·0099906	122·46	122·37	— 0·001

Sodium Chloride.

Concentration.	Λ observed.			Correction.
	Series (a)	Series (b)	Series (c)	
0·0001037	108·03	108·09	108·18	+ 0·013
0·0002053	107·80	107·80	107·81	+ 0·014
0·0005116	107·18	107·15	107·12	+ 0·019
0·0010180	106·46	106·49	106·45	+ 0·020
0·0020158	105·54	105·55	105·52	+ 0·013
0·005023	103·76	103·80	103·75	+ 0·011
0·009906	101·96	101·96	101·92	— 0·001

So much then, for the matter of " smoothed " values. Mr. Davies (loc. cit.[4], p. 82) goes on to say " in using such a method the weight con-

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[5] Kohlrausch, Ges Abh , 11, 888, 1911 "Abrundung der Konzentrationen. Um das Ganze ubersichtlich zu gestalten, ist nun noch übrig, die Aquivalentleitvermögen von den Konzentrationen, die sich bei den Pipettenverdünnungen ergeben haben und die den Werten 0·0001, 0·0002 usw. liegen, auf genau diese Konzentrationen reduzieren. Dies ist mit voller sicherheit möglich. Den die Kurven der Λ verlaufen so regelmässig, dass man überall die Tangente anlegen und mit deren Hilfe der Korrektion bestimmen kann. Die Rechnung vereinfacht sich noch dadurch, dass die wirklichen Konzentrationen untereinander gleich sind."

sciously or unconsciously assigned to each point in drawing the first curve is reflected in the result of the second, so that the process as a whole is not reproducible in the hands of different workers."

We find it difficult to attach any meaning to this sentence—we presume that in plain English it amounts to an assertion that no two workers, be they skilled in curve drawing or not, can draw practically identical curves through a series of good experimental points. Whatever Mr. Davies' criticism may mean, it applies with equal force to his own straight line plots, of which we may say, almost in his own terms, " the weight consciously or unconsciously assigned to each point in drawing a straight line is reflected in the value of the slope and intercept of that line so that the process as a whole is not reproducible in the hands of different workers." However, *solvitur ambulando*. Three independent sets of observers were furnished with Kohlrausch and Maltby's values for aqueous solutions of sodium chloride at 18° C. [6] and were asked to draw the appropriate curves. The values of " n " in equation (1) deduced from these curves were 0·456, 0·463, and 0·457 respectively, that is, to two significant figures, the results of three independent observers agreed in giving " n " equal to 0·46. The same observers were good enough to work out the value of " n " for potassium iodide dissolved in benzonitrile at 25° C., Dr. Martin's actual experimental figures being employed. The values of " n " obtained by them were 0·620, 0·610, and 0·617. Dr. Martin gives 0·637 (*loc. cit* [2], p. 3282) as the value of " n ." This, we trust, sufficiently disposes of the question of the reproducibility of our results.

Mr Davies states that " even where plentiful data are available at low concentrations n cannot be determined within narrow limits " and further asserts that our value of 0·452 for potassium chloride at 18° C. is " obviously not incompatible with the square-root rule." Let us examine the evidence on which these statements are based.

In the first place Mr. Davies, doubtful of our method, seeks to improve matters by reverting to a variant of the trial and error methods employed by earlier workers in this field and now abandoned. [7] Writing equation (1) in the form

$$\Lambda_0 - \Lambda = BC^n,$$

he gives various arbitrary values to Λ_0, and then plots logarithmically $\Lambda_0 - \Lambda$ against C. He finds that the results for hydrochloric acid are best represented by a straight line when Λ_0 is chosen at 427·2 and then $n = 0·5$. Other values of Λ_0 give what Mr. Davies assumes to be straight lines over a more limited range. Indeed he specifically states that the curves " show how widely n may vary while the data still obey the equation within the possible limits of experimental error " (*loc. cit.* [4], p. 84). Obviously if $n = 0·5$ is correct and gives a rectilinear plot, other values of n may be expected to give curvilinear plots, which indeed they do.

On the available data for hydrochloric acid the value 0·5 is reasonably correct, and here we have to apologise for having, however innocently, misled Mr. Davies. We ourselves found for hydrochloric acid that n

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[6] The figures given were the experimental values of series (*b*) uncorrected for small changes in temperature.

[7] Noyes, *J. Amer Chem Soc*, **30**, 335, 1908 ; Noyes and Falk, *J. Amer. Chem. Soc.*, **34**, 454, 1912 , Lorenz, *Z. anorg. Chem.*, **108**, 191, 1919 , Walden, *Z. anorg. Chem.*, **115**, 49, 1921.

was nearly unity (0·976).[8] This indicates that this acid obeys Ostwald's dilution law. Now Parker himself[9] supposed that it obeyed this law, and smoothed his results, making this assumption. (This of course, is an example of smoothing which prejudges the results.) As we used Parker's smoothed figures, it is not surprising that an approximation to Ostwald's law appeared in our final figures. We have redrawn the curves using the experimental figures. The $\Lambda - C$ curve is, on account of the irregularities in the experimental figures, difficult to draw, and the derived curve between log $\Delta\Lambda$ and log C is one of the few we have met with which shows a slight but appreciable curvature, indicating that equation (1) may not best represent the result. If, however, we draw a straight line through the mean position of the points, the slope of this line indicates a value of n lying between 0·5 and 0·6 in agreement with Mr Davies' result. Further than this we do not propose to go at present in discussing the characteristic equation for hydrochloric acid. The experimental data need revision, and one of the authors (A. I. V.) hopes to attack the problem in the near future.

Similar remarks apply to iodic acid. It is definitely recognised (loc. cit.[4], p. 68) that this acid does not conform to the square root law. We have recalculated the constants for this acid employing Kraus and Parker's experimental figures and find that

$$\Lambda_0 = \Lambda + 2187\ C^{0·880}.$$

The results are collected in Table II. and lead to a mean value for Λ_0 of 389·61.

TABLE II.—Iodic Acid, 25° C.

Run 2.								
$C \times 10^6$	5·37	13·11	23·25	41·07	68·20	110·97	--	—
Λ	388·67	388·80	388·30	387·50	386·04	384·08	—	—
Λ_0	389·05	389·04	389·60	389·80	389·63	389·59	—	—
Run 3								
$C \times 10^6$	6·644	14·22	25·17	43·95	70·34	110·33	—	—
Λ	389·05	388·54	388·10	387·21	385·96	384·22	—	—
Λ_0	389·51	389·45	389·68	389·65	389·65	389·70	--	—
Run 4.								
$C \times 10^6$	6·852	14·46	23·33	39·92	64·87	98·00	149·43	211·11
Λ	389·02	388·94	388·31	387·46	386·12	384·54	382·36	380·00
Λ_0	389·50	389·86	389·71	389·70	389·55	389·51	389·52	389·70
Run 5								
$C \times 10^6$	9·020	16·83	28·63	46·52	71·00	102·34	152·81	210·32
Λ	389·02	388·62	388·04	387·00	385·76	384·31	382·26	380·00
Λ_0	389·66	389·67	389·71	389·57	389·48	389·44	389·50	389·70

But perhaps the most interesting justification of the method which we employ is to be obtained from a study of Weiland's measurements[10] on potassium chloride at 18° C. It involves putting the method to a test to which it was never intended that it should be subjected, for the range of concentration is very small and the measurements are irregularly spaced as the figure given below shows. There is, for example, a large gap between $C = 1 \times 10^4$ and $C = 10 \times 10^{-4}$, which makes it difficult to draw accurately the $\Lambda - C$ curve. Weiland has given five series of measurements, details of which are given in Table III.

[8] Phil. Mag., 4, 300, 1927.   [9] J. Amer. Chem. Soc., 45, 2017, 1923.
[10] J. Amer. Chem. Soc., 40, 146, 1918.

TABLE III.

Series 1.		Series 2.	
$C \times 10^6$	Λ	$C \times 10^6$	Λ
23·958	129·490	7·4945	129·268
46·129	129·368	26·467	129·547
81·343	129·141	42·251	129·351
119·574	128·938	74·563	129·149
183·019	128·720	102·58	129·005

Series 4.

$C \times 10^6$	Λ	Λ_0
23·821	129·513	129·85
58·647	129·315	129·88
103·837	129·080	129·88
1021·87	127·224	130·28

Series 5.

$C \times 10^6$	Λ	Λ_0
31·951	129·430	129·83
61·944	129·166	129·75
123·36	128·911	129·79
958·22	127·312	130·26

Series 6.

$C \times 10^6$	Λ	Λ_0
26·960	129·369	129·75
60·878	129·125	129·74
104·17	128·926	129·77
154·14	128·733	129·80
236·09	128·510	129·88
1299·02	128·869	130·58

Mr. Davies, employing on each of these series the trial and error method described above, finds $n = 0·64$, $0·66$, $0·51$, $0·44$, and $0·39$ (*loc. cit.*,[4] p. 84). After quoting these results he remarks that " even where plentiful data are available at low concentrations n cannot be determined within narrow limits."

We do not propose to criticise Mr. Davies' deductions from these results.

If we examine Weiland's figures more closely, we find that two of the series are so irregular as to make it impossible to draw any deductions of quantitative value. For the other three series it is possible to draw reasonably good curves, and Fig. 1 shows that the straight lines obtained by the logarithmic plotting of $\Delta\Lambda$ and C are quite unambiguous. From these curves we obtain the values in Table IV. :

TABLE IV.

Series.	n.	B.	Λ_0.
3	0·587	174·6	129·9
4	0·587	174·6	129·8
5	0·585	181·9	129·8

We do not stress these figures as giving the best absolute value of n and Λ_0—the difficulties of experiment at these low concentrations are far too great—but the consistency of the results shows clearly that it *is* possible when data are available at low concentrations to determine n within narrow limits. As the matter is not unimportant we tabulate the relevant data so that the results may be checked. (Table V.)

TABLE V.

Series 3 and 4.

$C \times 10^6$	Λ	$\Delta\Lambda$	$\log \Delta\Lambda$	$\log C$	Λ_0
2	129·50	0·13	$\bar{1}$·11394	$\bar{5}$·30103	129·80
4	129·37	0·23	$\bar{1}$·36173	$\bar{5}$·60206	129·83
8	129·14	0·38	$\bar{1}$·57978	$\bar{5}$·90309	129·83
16	128·76	0·52	$\bar{1}$·71600	$\bar{4}$·20412	129·79
32	128·24	0·64	$\bar{1}$·80618	$\bar{4}$·50515	129·79
64	127·60				129·93

$$\Lambda_0 = \Lambda + 174\cdot6\, C^{0\cdot537}$$

Series 5.

$C \times 10^6$	Λ	$\Delta\Lambda$	$\log \Delta\Lambda$	$\log C$	Λ_0
2	129·44	0·14	$\bar{1}$·14613	$\bar{5}$·30103	129·76
4	129·30	0·24	$\bar{1}$·38021	$\bar{5}$·60206	129·79
8	129·06	0·36	$\bar{1}$·55630	$\bar{5}$·90309	129·79
16	128·70	0·55	$\bar{1}$·74036	$\bar{4}$·20412	129·79
32	128·15	0·69	$\bar{1}$·83885	$\bar{4}$·50515	129·79
64	127·46	—	—	—	129·92

$$\Lambda_0 = \Lambda + 181\cdot9\, C^{0\cdot585}$$

$$\left[\begin{array}{l} \boxdot = \text{Run 3 and 4} \\ \circledcirc = \text{Run 5} \end{array} \right].$$

KCl 18° (Wieland, 1918).
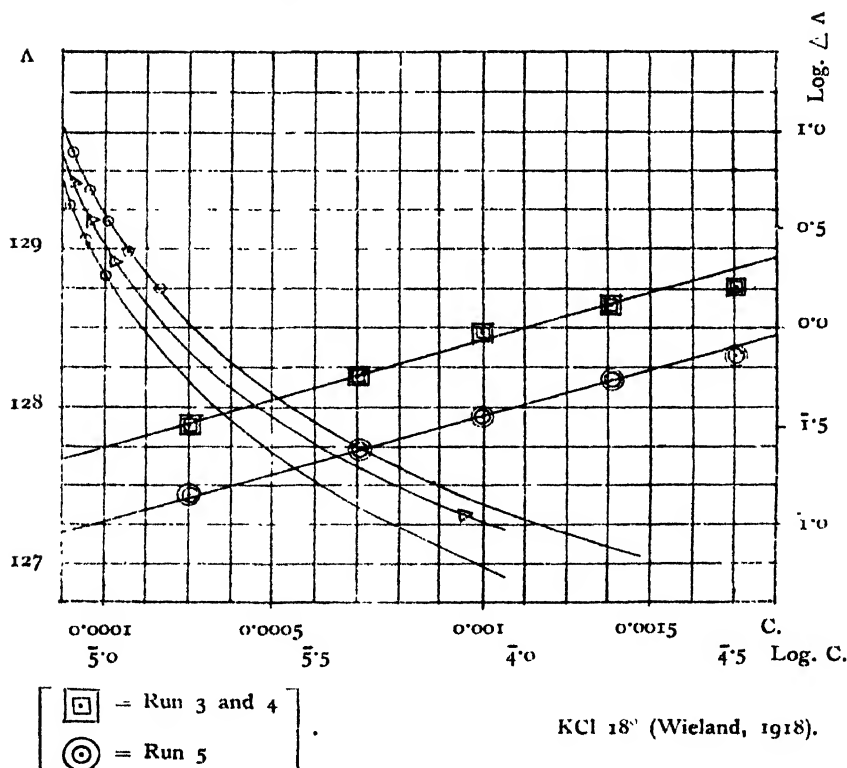
FIG. 1

Finally, as regards our general attitude we have little to add to the remarks made in a paper published in the *Transactions of the Faraday Society* some four years ago.[11] We do not reject the Kohlrausch square-root law—we simply enquire whether or not a given electrolyte follows the law. We do not "challenge the whole interionic theory." On the contrary we point out that there is a significant clustering of values

[11] *Trans. Faraday Soc.*, **23**, 404, 1927.

TABLE VI.—AQUEOUS SOLUTIONS.

Temperature.	Electrolyte.	Λ_0.	B.	n.
0° C.	KCl *	81·5	48·2	0·530
	NaCl *	66·7	83·4	0·657
	KNO₃ *	79·9	87·5	0·657
	KIO₃ *	60·7	111·7	0·715
	KClO₄ *	76·8	108·8	0·701
	LiClO₄ *	54·3	134·0	0·824
	K picrate *	55·1	114·1	0·748
18° C.	KCl	130·04	61·26	0·452
	NaCl	109·02	54·24	0·443
	LiCl	99·07	51·74	0·436
	KNO₃	126·39	74·67·	0·480
	NaNO₃	105·48	57·32	0·446
	LiNO₃	95·40	47·96	0·425
	KIO₃	98·54	61·07	0·460
	NaIO₃	77·54	54·66	0·455
	LiIO₃	67·53	48·22	0·442
	KBr	132·30	58·15	0·432
	KI	130·66	60·86	0·464
	KF	111·54	56·34	0·441
	NaF	90·08	62·69	0·483
	TlNO₃	127·39	113·10	0·546
	TlCl	131·04	152·73	0·576
	KCNS	121·08	74·35	0·495
	CsCl	133·07	80·97	0·506
	AgNO₃	116·19	64·17	0·440
	KClO₃	119·57	70·86	0·475
	Ca(NO₃)₂	114·02	100·63	0·420
	Sr(NO₃)₂	113·49	121·72	0·458
	Ba(NO₃)₂	116·87	175·63	0·512
	Pb(NO₃)₂	123·44	164·50	0·452
	CaCl₂	116·75	115·84	0·462
	MgCl₂	111·63	83·87	0·399
	RaBr₂ *	126·8	100·9	0·379
	K₂SO₄	132·85	141·98	0·458
	K₂C₂O₄	125·73	324·0	0·677
	MgSO₄	113·72	626·2	0·551
	CuSO₄	114·16	810·2	0·571
	CdSO₄	114·70	771·5	0·551
	ZnSO₄	114·26	608·5	0·527
	NaOH *	218·9	64·4	0·409
	LiClO₄ *	88·3	103·3	0·635
	K picrate *	89·7	53·8	0·460
	Na acetate *	76·0	95·9	0·649
25° C.	KCl	149·53	101·55	0·547
	NaCl *	128·1	59·5	0·409
	KBr *	153·3	72·1	0·438
	NaBr *	129·5	72·4	0·463
	KMnO₄ *	136·8	66·7	0·423
	Na acetate *	89·5	119·2	0·658
	K dichloroacetate *	122·5	44·8	0·171
	K trichloroacetate *	119·0	57·0	0·224
	Na trichlorobutyrate *	82·3	34·6	0·269
	Na ortho-nitrobenzoate *	83·8	54·2	0·400
	Na cyanoacetate *	92·9	35·9	0·261
	Na 3 : 5-dinitrobenzoate *	79·7	70·3	0·486
	Na ortho-chlorobenzoate *	86·8	31·6	0·241
	HIO₃	389·6	2187	0·880

Ionic Mobilities.

Temperature.	Cation.		Anion.	
0° C.	K+	40·3 *	Cl –	41·2 *
	Na+	25·5 *	NO$_3$–	39·5 *
	Li+	17·8 *	IO$_3$–	20·3 *
	Cs+	43·5 *	ClO$_4$–	36·5 *
			Picrate–	14·7 *
18° C.	K+	64·60	Cl –	65·54
	Na+	43·48	NO$_3$–	61·83
	Li+	33·53	IO$_3$–	34·00
	Tl+	65·53	Br –	67·70
	Cs+	67·53	I –	66·06
	Ag+	54·36	F –	46·77
	½ Ca++	52·19	CNS –	56·48
	½ Sr++	51·66	ClO$_3$–	54·97
	½ Ba++	55·04	ClO$_4$–	51·8 *
	½ Ra++	59·1	CH$_3$COO –	32·5 *
	½ Pb++	61·61	Picrate –	25·1 *
	½ Mg++	45·78	OH –	175·4
	½ Cd++	46·45	½ SO$_4$– –	68·25
	½ Zn++	46·01	½ C$_2$O$_4$– –	61·13
	½ Cu++	45·91		
25° C.	K+	74·5	Cl –	75·4
	Na+	51·4 *	Br –	77·9
			MnO$_4$ –	61·2 *
			CH$_3$COO –	38·0 *
			Dichloroacetate –	46·9 *
			Trichloroacetate –	43·4 *
			Trichlorobutyrate –	30·9 *
			Ortho-Nitrobenzoate –	32·4 *
			Cyanoacetate –	41·5 *
			3 . 5-Dinitrobenzoate –	28·3 *
			Ortho-Chlorobenzoate –	55·4 *

round 0·5 and it is possible that the exponent *n* is best represented by 0·5 $\pm$ δ, where δ is zero under the conditions of the Debye-Huckel theory.

Our main business, as we stated at the outset, is more pedestrian : we seek to obtain values as reliable as the existing data will permit of the constant Λ_0 and of the related ionic mobilities. We therefore take this opportunity to collect the values of Λ_0, *B*, *n*, and the ionic mobilities (for aqueous solutions) previously calculated. In these Tables we have corrected one or two slips which it is almost impossible to avoid in dealing with such a large mass of figures. The mobility of the hydrogen-ion has been omitted from the Tables ; revised figures for this important constant at 18° and 25° C. will be published in the near future by one of us (A. I. V.) in collaboration with Mr. G. H. Jeffery.

The experimental figures for Λ at different concentrations are of very variable value, and we have attempted in Table VI. to discriminate between the results obtained. Thus, for the substances asterisked the values of Λ_0, *b* and *n*, and the corresponding values of the ionic mobilities calculated therefrom, must not be regarded as more than first approximations in view of the uncertainty attaching to the experimental figures. It is doubtful, *e.g.*, whether the accuracy of the figures for KCl, NaCl, KBr, NaBr, and KMnO$_4$ at 25° C. (*Z. anorg. Chem.*, **116**, 161, 1921) exceeds 1 per cent. The results for KCl at 25° C. are deduced from unpublished observations made by Mr. G. H. Jeffery and one of us (A. I. V.).

REVIEWS OF BOOKS

The authors' thanks are due to Mr. G. H. Jeffery, B.Sc., for much assistance in the calculations, to Messrs. A. E. Clarence-Smith, M.A., C. H. Beale, B.Sc., and L. G. Carpenter, B.A., B.Sc., for drawing the curves for sodium chloride and potassium iodide, and to the Royal Society for a grant to one of them (A. I. V.).

East London College,
(University of London),
London, E.1,
and University College,
Southampton.

REVIEWS OF BOOKS.

Electrolytic Conduction. By F. H. NEWMAN. (London : Chapman & Hall, 1930. Pp. xii + 441. Price 25s. net.)

Professor Newman's book is written from the point of view of the physicist but is equally suitable for students of chemistry and physics and for research workers in both fields. It will also prove a useful reference book for technical experts and, generally, for all who require information on the modern aspects of the theory of electrolytic dissociation and electrolysis. It contains a very complete account of the more modern developments of the subject, including a full mathematical discussion of the theory of Debye and Huckel on electrolytic conduction in solutions of strong electrolytes, but the older researches are also dealt with in a satisfactory manner. There are numerous references and tables of results, which make the book especially useful to the more advanced reader, whilst the treatment of the fundamental parts of the subject should be well within the capacity of the average student. In such a large field the choice of material appears to be good, and concentration cells and other types of cell are dealt with. The section on concentration cells, in particular, gives an unusually clear account of a subject which often gives difficulty to students. Very few errors, of a minor character, have been noted. The statement on p. 6 that the diminution of thermodynamic potential gives the free energy change at constant pressure is a common error with students. If the free energy change is defined as giving the maximum work, as is usual, the work done, whether at constant pressure or not, is always equal to the diminution of the true free energy $(u - Ts)$; the diminution of thermodynamic potential $(u - Ts + pv)$ giving the maximum work minus the external work, $p(v_2 - v_1)$. On p. 8 the expression $\partial p/\partial T$ in the Clausius equation should be replaced by dp/dT, since p is a function of T alone. The name Bülmann is given instead of Biilmann on p. 201. The book is one which should prove very useful and interesting to a wide circle of readers.

J. R. P.

Thermodynamics. By A. W. PORTER, D.Sc., F.R.S. Methuen's Monographs on Physical Subjects. (London : Methuen & Co., Ltd. Pp. vii + 96. 22 diagrams. Price 2s. 6d.)

To condense the fundamentals of Thermodynamics, together with a reasonably wide choice of examples of the applications of the subject, into a space of less than a hundred pages is no small achievement, and one which would not be

possible except with an author thoroughly at home with his subject. That Professor Porter has been able to do this successfully will not surprise those who know his capacity for concentration on essentials, and that the text is both clear and readable is also what one would expect of the author. Although the book is one of a series which professes to treat of physical subjects, it deals with many of the applications of thermodynamics to chemistry and will be equally useful to chemists. There is no attempt to treat the subject without the necessary mathematical apparatus, but this is restricted to those parts of the calculus which are known by the majority of students of chemistry. Some parts of the discussion are more detailed than the rest, such for example as those dealing with the characteristic equation and with solutions, in both of which fields the author has made important original contributions. For this reason many readers who are already acquainted with the subject will find the book useful, whilst to those beginning the study of the subject Professor Porter's account will make clear a number of difficulties they will probably encounter. It will be found most useful whatever other sources of information are drawn upon by the reader. The treatment of the thermodynamic functions is especially to be commended, and since the use of these functions is becoming more and more general in practical thermodynamics, such a clear account is to be welcomed.

Photochemistry. By D. W. G. STYLE, Ph.D. : with a preface by Professor A. J. ALLMAND, M.C., D Sc., F.R.S. Methuen's Monographs on Physical Subjects. F'scap 8vo. Pp. vii + 96. With 9 diagrams. (London Methuen & Co., 1930. Price 2s. 6d. net.)

This book is an intruder into a physical series of monographs, but the intrusion may be welcomed, for, as Professor Allmand says in his preface "the subject is one abounding in interest to the physicist." As soon as the chemist realised the value of the new physical theories he began to apply them with conspicuous success to his own problems. The foundation of the new advance is Planck's discovery in 1900 that radiation takes place in jerks or quanta ; its first application to chemical changes was made by Einstein in 1912 who laid it down that one light-absorbing molecule should react for each quantum of radiation absorbed. The quanta are of many kinds—in each case being proportional to the frequency of the radiation. The radiation that an atom can absorb is of many types, for each atom is a complicated system, consisting of many " states " (to avoid a more materialistic specification) for which the energy-content is different, and it is assumed that the energy is only absorbed in so far as it can effect a change of "state" of the atom (or group) upon which it is incident. This energy absorbed is a kind of latent heat, but it differs from ordinary latent heats owing to this multiplicity of values for the same atom and also in being independent of temperature. The atom so activated by light is assumed to be more capable of chemical action and to initiate whatever chemical changes the system is capable of undergoing. These turn out in most cases to be complicated and hence the need of a monograph such as this in which an outline of the subject can be presented. When a bull, dazzled by light, is turned loose in a china shop many things may happen. When an atom is excited by light many things may happen in a chemical mixture. Dr. Style presents a very critical account, not attempting to hide the many difficulties that arise in fitting in hypothetical reactions so as to account for the changes that can be observed experimentally. The most obvious difficulty is that in many cases Einstein's law appears to be violated, the yield being 1000 or 100,000 times the value expected by it. It is assumed at the

present time that the primary action of the light satisfies the law, but that the excited atom can in turn initiate other changes which add to the final effect. The various possibilities are discussed   The photo-combination of hydrogen and bromine is considered in full and the results are at least fairly satisfactory   The similar problems for hydrogen and chlorine is still under discussion as is shown by the recent debate on the subject at Liverpool.

Dr. Style is a clear expounder and is obviously intimately acquainted with every detail of the subject.   Probably there are few workers who will not learn something from the book in spite of its compression into less than 100 pages.

There is a final chapter on Experimental methods.

Rapports sur les Hydrates de Carbone (Glucides).   Dixième Conférence de l'Union Internationale de Chimie, 1930.   (Paris.   Pp. 286.   Price,   .)

The tenth meeting of the *Union Internationale de Chimie*, held in Liége in September, 1930, was made the occasion for the presentation and discussion of a series of " Reports on Carbohydrates," which have now been published.   The reports fall under three headings as follows : (A) Chemical Constitution of the Sugars : (1) History of the Oses since Emil Fischer, by G. Bertrand, (2) Ring-structure in the Mono-, Di-, and Polysaccharides, by W. N. Haworth, (3) Rotatory Power of the Sugars, by C. S. Hudson, (4) Mutarotation, by T. M. Lowry and G. F. Smith ; (B) Polysaccharides : (5) Starch and its Degradation Products, by A. Pictet, (6) Structure of the Polysaccharides, by P. Karrer, (7) Molecular Weight of Complex Polysaccharides, by H. Pringsheim, (8) Application of Röntgen Rays and the study of Polysaccharides and their Derivatives, by H. Mark ; (C) Applications of Cellulose : (9) Relation between Cellulose Properties and its Industrial Applications, by E. Hauser, (10) Colloidal State of Cellulose and its derivatives, by D. Duclaux, (11) Physical Properties of Artificial Silk, by E. Viviani.

These eleven reports are printed in the language of origin, namely, four in English, three in French, three in German, and one in Italian.   The names of those who contributed to the discussions are given, but the discussion itself is not reported.   The organisation of a scientific meeting alongside the administrative work of the Union was a novelty which appears to have been fully justified. The reports from Germany, which were a landmark in the process of restoring international relationships in Chemistry, contributed substantially to the success of the venture.   The German contributions would have been even more valuable, but for a misunderstanding which limited the German visitors to the official delegation, instead of including also those eminent sugar-chemists, wh) had not been invited to present reports, but were expected to attend and take part in the discussions.

T. M. L.

ERRATUM.

May Number, p. 207, formula (6) :—

for

$$c^2 = \frac{r^2}{\cos^2 i}\left[1 - \frac{c^2}{3\beta^2} \cdots \right.$$

read

$$c^2 = \frac{r'}{\cos^2 i}\left[1 - \frac{2c^2}{3\beta^2} \cdots \right.$$

A STUDY OF AQUEOUS SALT SOLUTIONS IN EQUILIBRIUM WITH SOLID SECONDARY CALCIUM PHOSPHATE AT 40° C.*

By Joseph W. H. Lugg.

(*From the Nutrition Laboratory of the Council for Scientific and Industrial Research, University of Adelaide, South Australia.*)

The objects of this study were :—

1. To find which solid secondary calcium phosphate is stable in con tact with aqueous salt solutions at 40° C.

2. From analyses of solutions in equilibrium contact with the parti cular secondary calcium phosphate, to determine the stoichiometri solubility products of that salt, and further, to find to what exten the results might be explained in the light of modern theory, partl with a view to allowing their more extensive employment in solubilit calculations.

The Solid Secondary Calcium Phosphate in Equilibrium with Aqueous Salt Solution at 40° C.

There are two well-defined secondary calcium phosphates, namely " brushite " ($CaHPO_4$, $2H_2O$), and " monetite " ($CaHPO_4$). The forme is said to crystallise in the monoclinic system, the latter in the triclinic

Cameron, Seidell, and Bell [1] claim that only a series of solid solution exists between the pure solids, secondary calcium phosphate and lime but the work of Bassett [2] indicates the existence of at least two inter mediate molecular species, $Ca_3(PO_4)_2$ and $3Ca(PO_4)_2$, $Ca(OH)_2$. Ii general the calcium phosphates are hydrolysed by water, the liquic phase tending to become more acidic and the solid more basic, anc Bassett maintains that hydroxy-apatite alone is stable in contact witl faintly acid, neutral, and alkaline solutions. Despite a surviving doub as to its existence as a chemical entity, $Ca_3(PO_4)_2$ has been involved ii several biochemical studies in recent years.

From Bassett's phase diagram it would appear that brushite ma} co-exist with $Ca_3(PO_4)_2$ and water, only below 36° C., whilst at highe temperatures monetite replaces the brushite at equilibrium. Bassett' dilatometer results indicate that the transition temperature could hav been determined only approximately. Holt, La Mer, and Chown

[1] *J.A.C.S.*, **27**, 1503 and 1512, 1905.   [2] *Z. anorg. Chem.*, **59**, 29, 1908.
[3] *J. Biol. Chem.*, **64**, 509 and 567, 1925.

have shown that brushite may remain in equilibrium with aqueous solutions at 38° C. As the present study deals with systems at 40° C., it was necessary to find which salt, brushite or monetite, would be stable in contact with solutions at this higher temperature.

Calcium phosphate (analysis indicated about 25 per cent. brushite, 70 per cent. monetite, and a little of a more basic salt, here assumed to be $Ca_3(PO_4)_2$) was dissolved in a very slight excess of hydrochloric acid and the solution was kept at 40° C. Sodium hydroxide solution at the same temperature, was then added with shaking, but the liquid in contact with the precipitate was left acid to litmus. The fine crystals, deposited in the form of an almost gelatinous precipitate, were identified as brushite from their appearance under the microscope and from the loss of weight upon ignition to calcium pyrophosphate.

Later work in which brushite was shaken with water and salt solutions at 40° C., under which conditions small amounts of a more basic salt (supposedly $Ca_3(PO_4)_2$) must have been present, showed that the brushite was not converted to monetite. A mixture of brushite and monetite neither gained nor lost water on being shaken with water at 40° C. for seven days. Hydration of monetite at this temperature must therefore be very slow.

From the evidence at hand it was inferred that brushite and $Ca_3(PO_4)_2$ (if this be the more basic solid) may co-exist with an aqueous liquid phase at temperatures up to at least 40° C., and that the secondary calcium phosphate precipitated from aqueous solutions at 40° C. is brushite.

Theoretical Discussion of the Solubility of Brushite and the Dissociation Constants of Phosphoric Acid.

The following symbols have been employed :

$[X]$ is the concentration of X in moles per litre. (*e.g.* $[H^+]$).

a_X is the activity of X (*e.g.* a_{H+})

γ_X is the activity coefficient of X, where $a_X = \gamma_X[X]$

p signifies negative common logarithm.

$K_{sp\ salt}$ is the stoichiometric solubility product of a salt.

$K'_{sp\ salt}$ is the activity solubility product of a salt.

$K_1, K_2, K_3,$ are the stoichiometric dissociation constants of H_3PO_4.

$K_1', K_2', K_3',$ are the activity dissociation constants of H_3PO_4.

z_i is the valence of ions of kind i.

μ is the " ionic strength " as defined below in the text.

Other symbols are defined as they occur in the text.

Hydrolysis, in the experimental work to be considered, must have left a more basic solid with the original brushite. There is some doubt whether this substance could have formed solid solutions with the brushite, as discussed in the first division, but even if it did, the calculated extents of hydrolysis show that the brushite concentrations in the solid phases could not have suffered appreciable decrease. At constant temperature then, the solid brushite activity must have been sensibly constant and so therefore must $K'_{sp\ brushite}$ in the liquid phases. $K_{sp\ brushite}$ varied with the ionic environment. In accordance with the Complete Dissociation Theory $[Ca^{++}]$ has been assumed equal to $[Ca]$ determined analytically. The $[HPO_4^=]$ was calculated from the total phosphate

molarity, [total P], and the dissociation constants of H_3PO_4. We have for brushite :—

$$p_{K_{sp}} = p[Ca^{++}] + p[\text{total P}] + p\frac{[HPO_4^-]}{[\text{total P}]} \qquad . \qquad . \quad (1)$$

The Debye-Hückel[4] equation connecting the activity coefficient of an ion with the ionic environment was developed upon the assumption that inter-ionic effects alone are responsible for the departure of γ from unity. Where γ_i is the activity coefficient and z_i the valence of an ion of kind i, z the valence and C the concentration in moles per 1000 c.c. of any particular ion in the ionic environment, and b_i is a mean limit of radial approach of ions to ions of kind i, the equation is :—

$$p\gamma_i = \frac{Az_i^2\sqrt{\frac{1}{2}\Sigma(Cz^2)}}{1 + Bb_i\sqrt{\frac{1}{2}\Sigma(Cz^2)}} \qquad . \qquad . \qquad . \qquad (2)$$

$\Sigma(Cz^2)$ is frequently replaced by 2μ, where "μ" is the "ionic strength" as defined by Lewis and Randall,[5] but it is clear that C, signifying moles per 1000 c.c., is replaced better by "molarity" than by "molality," and throughout the paper, μ has been calculated from the definition, $\mu = \frac{1}{2}\Sigma([\text{ion } i]z_i^2)$. If the nature of the ionic environment is not changed, b_i remains constant for all values of μ.

The values of the additional "salting out" term in the more general equation derived by Hückel,[6] are usually so small at values of μ below unity that this term has not been included in the practical equation, (3), applied to the data recorded herein.

$$p\gamma_i = \frac{Az_i^2\sqrt{\mu}}{1 + Bb_i\sqrt{\mu}} \qquad . \qquad . \qquad . \qquad (3)$$

For water, $A = 0.49$ at $0°$ C., 0.50 at $20°$ C., and 0.52 at $40°$ C. ; whilst B has the values 3.24, 3.28, and 3.30 respectively.

Equation (3) may be applied to account for the variation of $K_{sp\ brushite}$ with μ, $K'_{sp\ brushite}$ remaining constant. Thus :—

$$K_{sp} = [Ca^{++}] [HPO_4^-] \text{ and } K'_{sp} = a_{Ca^{++}} \cdot a_{HPO_4^-}, \text{ whence :}$$

$$p_{K'_{sp}} - p_{K_{sp}} = p\gamma_{Ca^{++}} + p\gamma_{HPO_4^=} \qquad . \qquad . \qquad (4)$$

For the Ca^{++} ion let the collective coefficient of $\sqrt{\mu}$ in the denominator of equation (3) be denoted by c, and for the $HPO_4^=$ ion let d denote the coefficient. Substituting in equation (4), and introducing the numerical value of A at $40°$ C. :—

$$p_{K'_{sp}} - p_{K_{sp}} = 4.15\sqrt{\mu}\left[\frac{1 + \dfrac{c\sqrt{\mu} + d\sqrt{\mu}}{2}}{(1 + c\sqrt{\mu})(1 + d\sqrt{\mu})}\right] \qquad . \qquad (5)$$

where c and d are constant for a particular foreign salt.

For practical purposes equation (5) may, as a rule, be reduced to :—

$$p_{K'_{sp}} - p_{K_{sp}} = \frac{4.15\sqrt{\mu}}{1 + c\sqrt{\mu}} \qquad . \qquad . \qquad . \qquad (6)$$

where c now has some mean value.

[4] Physik. Z., 24, 185, 1923.
[5] "Thermodynamics," McGraw-Hill Book Co., N.Y., 373, 1923.
[6] Physik. Z., 26, 93, 1925.

As $\sqrt{\mu}$ approaches zero, equation (6) reduces to the Brönsted-La Mer form :—

$$p_{K'_{sp}} - p_{K_{sp}} = 4 \cdot 15\sqrt{\mu} \quad . \quad . \quad . \quad . \quad (7)$$

It was proposed to study the variations of $p_{Ksp \text{ brushite}}$ as a function of $\sqrt{\mu}$ in various salt solutions. From equation (1) it will be seen that this requires, among other things, a determination of $[HPO_4^=]/[\text{total P}]$. The following considerations show how this may be carried out.

The Fraction of Total Phosphate in Solution Existing as $HPO_4^=$ Ion.

We have :—

$$[\text{Total P}] = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^=] + [PO_4^\equiv] \quad . \quad (8)$$

The antilogarithm of $-p_H$ may be taken as a close approximation to a_{H^+}, but it is more consistently represented by H. In the following considerations, the important fact is that $\dfrac{H}{[H^+]}$ will be constant, provided the ionic environment does not vary appreciably as $[H^+]$ is varied, and this condition obtains when a foreign salt dominates the situation. The dissociation constants $\bar{K}_1$, $\bar{K}_2$, $\bar{K}_3$, are defined in equations, (9), (10), and (11) given below. From these it is clear that

$$\bar{K}_1 = K_1\frac{H}{[H^+]}, \quad \bar{K}_2 = K_2\frac{H}{[H^+]}, \quad \text{and} \quad \bar{K}_3 = K_3\frac{H}{[H^+]}.$$

$$\bar{K}_1 = \frac{H[H_2PO_4^-]}{[H_3PO_4]} \quad . \quad . \quad . \quad . \quad (9)$$

$$\bar{K}_2 = \frac{H[HPO_4^=]}{[H_2PO_4^-]} \quad . \quad . \quad . \quad . \quad (10)$$

$$\bar{K}_3 = \frac{H[PO_4^\equiv]}{[HPO_4^=]} \quad . \quad . \quad . \quad . \quad (11)$$

With equation (8), these yield :

$$\frac{[HPO_4^=]}{[\text{total P}]} = \frac{H\bar{K}_1\bar{K}_2}{H^3 + H^2\bar{K}_1 + H\bar{K}_1\bar{K}_2 + \bar{K}_1\bar{K}_2\bar{K}_3} \quad . \quad . \quad (12)$$

The orders of magnitude of $\bar{K}_1$, $\bar{K}_2$ and $\bar{K}_3$ are such that the first and last terms in the denominator of equation (12) are negligible in comparison with the remaining pair over the p_H range, 4·5 to 7·5. Equation (12) thus reduces to :

$$\frac{[HPO_4^=]}{[\text{total P}]} = \frac{\bar{K}_2}{H + \bar{K}_2} \quad . \quad . \quad . \quad . \quad (13)$$

This p_H range obtained in the solutions saturated with respect to brushite. To determine $[HPO_4^=]/[\text{total P}]$, it was therefore necessary to evaluate $\bar{K}_2$ as far as possible in the same salt solutions as used for the main experiments, and substitute it with H in equation (13).

The p_H's of salt solutions in equilibrium with brushite were determined with the aid of the quinhydrone electrode at 25° C., and $p_{\bar{K}_2}$ values in solutions of the same foreign salts were obtained in the same way at 23·5° C. Provided that p_H varies inappreciably between these temperatures, it may be shown that corrections to 40° C. balance out in the cal-

culation of $\dfrac{[HPO_4^=]}{[total\ P]}$ and therefore need not be applied. From the work of Hastings and Sendroy,[7] temperature variation of p_H between 23·5° C. and 25° C. would be negligibly small. Quinhydrone salt-error is known for some of the foreign salts concerned in this study, but junction potentials are not known. Except in checking the electrical system with the p_H standard solution, no attempt was made to apply corrections for these errors. They are quite small, and it may be shown that they balance out exactly in the calculation of $[HPO_4^=]/[total\ P]$. To be consistent, one might substitute " uncorr. H " and "uncorr. $\overline{K}_2$" for H and $\overline{K}_2$ respectively, in equation (13). Henceforth, uncorrected values are meant when the terms, p_H and $p\overline{K}_2$, occur in the paper.

Materials, Apparatus, and Analytical Methods Employed.

Pyrex vessels and Merck's guaranteed reagents were employed where possible. Brushite for the solubility experiments was prepared by precipitation methods discussed in the first division, washed with dilute H_3PO_4 and finally with water, and dried in the air. Ignition to pyrophosphate was accepted as a test for purity.

p_H **Determination**: p_H was determined electrometrically with the aid of the quinhydrone electrode connected with a $0·1N$ calomel half-cell by a bridge of saturated KCl in agar. A solution of $0·01M$ HCl in $0·09M$ KCl was employed as a p_H standard of value 2·076 between 23·5° C. and 25° C. Its junction potential against saturated KCl must be very small. The quinhydrone salt-error correction is $-0·009$ and was always applied.

Phosphate Estimation: The colorimetric method of Fiske and Subbarow[8] was employed. With respect to foreign salt concentration, the standard was always made similar to the test solution, and estimations were accurate to within 1 per cent.

Calcium Estimation: Calcium was estimated by precipitation as oxalate, followed by permanganate titration of the oxalate when taken up in acid. Micro-technique was followed and the error was found to be less than 3 per cent. In the presence of $MgSO_4$, three precipitations were necessary. Permanganate titrations were done after each and the close agreement between second and third titrations suggested that the error could not have been much greater than 3 per cent. In the presence of $CaCl_2$ semi-micro-technique was followed and the error was less than 2 per cent.

Sulphate Estimation: Sulphate was estimated by precipitation as $BaSO_4$, which was ignited and weighed. The method was accurate to within 1 per cent.

The Second Dissociation Constant $\overline{K}_2$ of Phosphoric Acid at 23·5° C.

In logarithmic form equation (10) becomes :

$$p\overline{K}_2 = p_H + p\dfrac{[HPO_4^=]}{[H_2PO_4^-]} \qquad . \qquad . \qquad . \quad (14)$$

For the nth dissociation (excepting the first) of a polybasic acid, where γ_a and γ_b are the activity coefficients of the dissociated and

[7] *J. Biol. Chem.*, 61, 695, 1924.   [8] *Ibid.*, 66, 375, 1925.

dissociating ions respectively, and p_H is assumed identical with pa_{H^+}, we have :

$$p_{K_n}' - p\bar{K}_n = p\gamma_a - p\gamma_b \qquad . \qquad . \qquad . \quad (15)$$

The ions are of valence z_c and z_d respectively, and $n = z_c = z_d + 1$.

Substitution of equation (3) in (15) gives :

$$p_{K_n}' - p\bar{K}_n = A(z_c^2 - z_d^2) \sqrt{\mu} \left[\dfrac{1 + \dfrac{z_c^2 d\sqrt{\mu} - z_d^2 c\sqrt{\mu}}{z_c^2 - z_d^2}}{(1 + c\sqrt{\mu})(1 + d\sqrt{\mu})} \right] \qquad . \quad (16)$$

For the second dissociation of H_3PO_4 at $23.5°$ C., equation (16) becomes :

$$p_{K_2}' - p\bar{K}_2 = 1.5\sqrt{\mu} \left[\dfrac{1 + \dfrac{4d\sqrt{\mu} - c\sqrt{\mu}}{3}}{(1 + c\sqrt{\mu})(1 + d\sqrt{\mu})} \right] \qquad . \quad (17)$$

When c and d are equal, and for practical purposes when the difference between them is not great, equation (17) may be reduced to (18), in which c now has some mean value.

$$p_{K_2}' - p\bar{K}_2 = \dfrac{1.5\sqrt{\mu}}{1 + c\sqrt{\mu}} \qquad . \qquad . \qquad . \quad (18)$$

In the limit, as $\sqrt{\mu}$ approaches zero, (17) and (18) both become

$$p_{K_2}' - p\bar{K}_2 = 1.5\sqrt{\mu} \qquad . \qquad . \qquad . \qquad . \quad (19)$$

Variations of the constant $p\bar{K}_2$ in presence of the salts NaCl, KCl, Na_2SO_4, $CaCl_2$, and $MgSO_4$, were investigated briefly. Values of $p\bar{K}_2$ were obtained by measuring the p_H's of salt solutions containing known small quantities of primary and secondary alkali metal phosphates, and substituting in equation (14). Assuming complete dissociation of strong electrolytes, [$H_2PO_4^-$] and [$HPO_4^=$] follow from the stoichiometric salt concentrations. It was calculated that the hydrogen ionisation of the phosphate fractions would not alter appreciably either [$H_2PO_4^-$] or [$HPO_4^=$].

One of the solutions containing $CaCl_2$ was made definitely undersaturated with respect to brushite whilst the [$H_2PO_4^-$] was left large enough to give the solution a low p_H and so reduce the risk of atmospheric CO_2 absorption. As the $p\bar{K}_2$ value agreed well with the values determined in the other $CaCl_2$ solutions, all of which were greatly supersaturated with respect to brushite, all the data for $CaCl_2$ appeared to be reliable.

The last five experiments listed in Table I. were made at $26°$ C., and at approximately constant ionic strength with NaCl, with the object of testing this application of the " mass law " to the second dissociation of H_3PO_4. They are sufficiently reassuring.

Results and Discussion.

The data are shown in Table I., which contains in the order of the columns : molarity of the particular primary phosphate, molarity of the particular secondary phosphate, molarity and nature of the foreign salt, μ, and $p\bar{K}_2$.

For solutions containing only equi-molar concentrations of the two

sodium phosphates, Cohn[9] has found that an equation of the form of (18), where $c = 1.65$, applies admirably to his own data and to those of other investigators. At 18° C. the p_{K_2}' values range between 7·14 and 7·18 with a mean of 7·16. Temperature correction makes this 7·15 at 23·5° C. Quinhydrone salt errors in the first and second experiments of Table I. must be very small, and when Cohn's equation is applied the value found for p_{K_2}' in each case is 7·15. $p_{\overline{K}_2}$ values from the first to the twenty-second experiment, inclusive, were plotted against $\sqrt{\mu}$ values as shown in Fig. 1, and there was no hesitation in extrapolating the curves to $p_{K_2}' = 7·15$.

TABLE I.—SECOND DISSOCIATION OF PHOSPHORIC ACID AT 23·5° C.

[Primary Phos.]	[Secondary Phos.]	[Foreign Salt.]	μ.	$p_{\overline{K}_2}$.
0·0100 NaH_2PO_4	0·0100 Na_2HPO_4	—	0·0400	6·92
0·0500 ,,	0·0500 ,,	—	0·2000	6·77
0·0100 KH_2PO_4	0·0100 ,,	—	0·0400	6·95
0·0020 NaH_2PO_4	0·0020 ,,	0·10000 NaCl	0·1080	6·70
0·0020 ,,	0·0020 ,,	0·20000 ,,	0·2080	6·59
0·0005 ,,	0·0005 ,,	0·20000 ,,	0·2020	6·60
0·0020 ,,	0·0020 ,,	0·80000 ,,	0·8080	6·30
0·0020 ,,	0·0020 ,,	0·10000 KCl	0·1080	6·75
0·0020 ,,	0·0020 ,,	0·20000 ,,	0·2080	6·67
0·0020 ,,	0·0020 ,,	1·00000 ,,	1·0080	6·48
0·0020 ,,	0·0020 ,,	0·02380 Na_2SO_4	0·0794	6·77
0·0020 ,,	0·0020 ,,	0·04760 ,,	0·1510	6·69
0·0020 ,,	0·0020 ,,	0·09520 ,,	0·2940	6·57
0·0020 ,,	0·0020 ,,	0·19040 ,,	0·5790	6·48
0·0020 ,,	0·0020 ,,	0·00406 $CaCl_2$	0·0200	6·72
0·0010 ,,	0·0002 ,,	0·00406 ,,	0·0138	6·81
0·0010 ,,	0·0010 ,,	0·01015 ,,	0·0340	6·61
0·0020 KH_2PO_4	0·0010 ,,	0·01015 ,,	0·0354	6·62
0·0005 NaH_2PO_4	0·0005 ,,	0·02030 ,,	0·0620	6·46
0·0050 ,,	0·0050 ,,	0·00980 $MgSO_4$	0·0592	6·67
0·0050 ,,	0·0050 ,,	0·02450 ,,	0·1180	6·48
0·0050 ,,	0·0050 ,,	0·09800 ,,	0·4120	6·16
0·0020 KH_2PO_4	0·0020 ,,	0·20000 NaCl	0·2080	6·61
0·0020 ,,	0·0010 ,,	0·20000 ,,	0·2050	6·62
0·0010 ,,	0·0020 ,,	0·20000 ,,	0·2070	6·57
0·0010 ,,	0·0010 ,,	0·20000 ,,	0·2040	6·60
0·0050 ,,	0·0050 ,,	0·20000 ,,	0·2200	6·56

Four of the curves are closely represented by equations (20), (21), (22) and (23), each of the form of (18), but the last three would not apply at low $\sqrt{\mu}$ values if the curves there actually cross the line, as do those of $MgSO_4$ and $CaCl_2$ at the higher $\sqrt{\mu}$ values.

$$NaH_2PO_4 = Na_2HPO_4 : \quad p_{\overline{K}_2} = 7·15 - \frac{1·5\sqrt{\mu}}{1 + 1·65\sqrt{\mu}} \qquad (20)$$

$$KCl \text{ as foreign salt}: \quad p_{\overline{K}_2} = 7·15 - \frac{1·5\sqrt{\mu}}{1 + 1·18\sqrt{\mu}} \qquad (21)$$

$$Na_2SO_4 \text{ as foreign salt}: \quad p_{\overline{K}_2} = 7·15 - \frac{1·5\sqrt{\mu}}{1 + 0·85\sqrt{\mu}} \qquad (22)$$

$$NaCl \text{ as foreign salt}: \quad p_{\overline{K}_2} = 7·15 - \frac{1·5\sqrt{\mu}}{1 + 0·60\sqrt{\mu}} \qquad (23)$$

[9] J.A.C.S., 49, 173, 1927.

If $c > d$, equation (16) always leads to a curve lying completely to the right of the limiting straight line, $p\bar{\mathrm{K}}_n = p\mathrm{K}_n' - A(z_o{}^2 - z_d{}^2)\sqrt{\mu}$ (*e.g.* the KCl curve drawn in Fig. 1). Depending upon the value of n, it may lead to a similar curve when $d > c$, but for other values of n, a curve of the CaCl$_2$ type will result. The curves for MgSO$_4$ and CaCl$_2$ in Fig. 1 are extremely interesting and may be explained with the aid
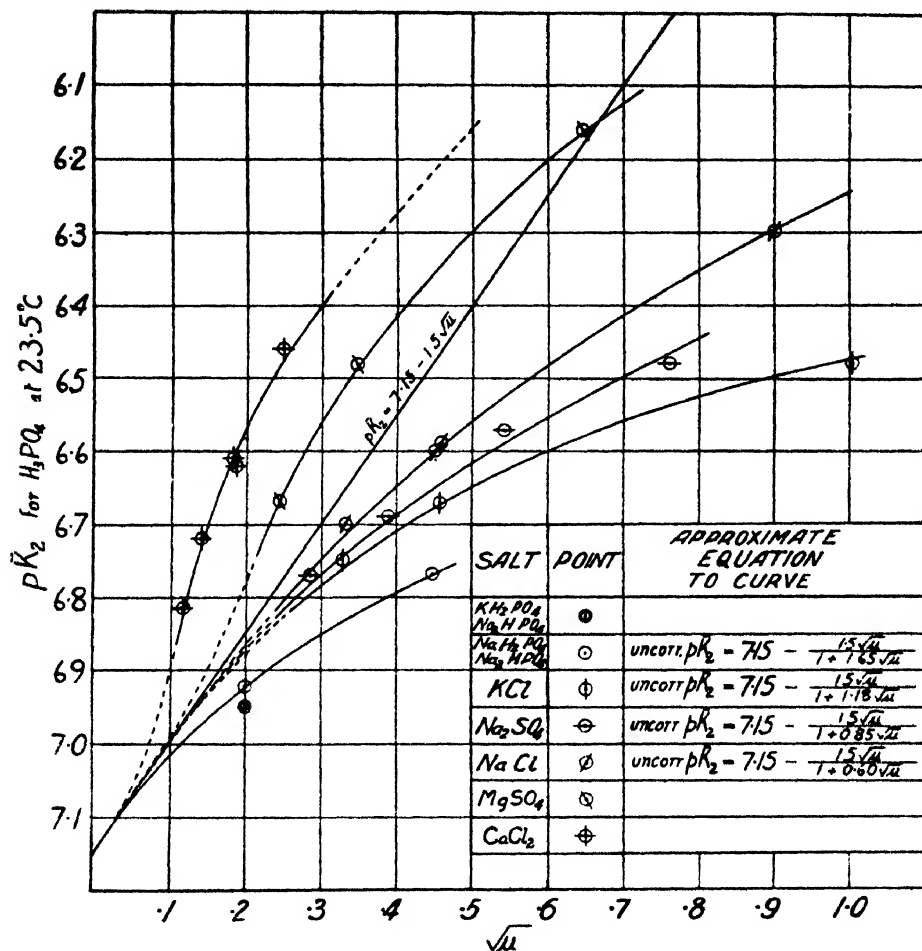
FIG. 1.

of equation (17), but it has been deemed impractical to evaluate c and d for these salts because the limits of ionic approach must be very close, a fact further borne out by the brushite solubility data, and Gronwall, La Mer, and Sandved [10] have shown that equation (3) has doubtful applicability in such cases. Furthermore, Onsager's [11] treatment of MgSO$_4$ conductivity data indicates that this salt is incompletely ionised, and the treatment accorded it here is consequently inadequate.

Michaelis and Kruger's [12] data for NaCl and KCl solutions agree closely with those in Table I. It appears that the effects of Na$_2$SO$_4$, CaCl$_2$, and MgSO$_4$, have not previously been investigated.

[10] *Physik. Z.*, **29**, 358, 1928.   [11] *Ibid.*, **28**, 277, 1927.
[12] *Biochem. Z.*, **119**, 307, 1921.

The Solubility Products of Brushite at 40° C.

50 mls. of water or of the foreign salt solution were shaken with excess of solid brushite at 40° C. in a thermostat. Immediately following removal from the thermostat, the liquid was rapidly filtered and did not cool more than 8° in the process. Further cooling did not make the filtrate cloudy. Part of it was reserved for analysis, and the remainder was used in p_H measurement at 25° C.

The first experiment was made with one gram of solid brushite and the shaking period was one day. Three grams of the same sample of brushite were employed in the second, the shaking period being seven days. In the third, three grams of a more coarsely crystalline preparation were employed and the shaking period was three days. From the results it was concluded that a two-day period would be the most satisfactory, although equilibrium with respect to brushite might be attained sufficiently well in one day. The two samples of brushite gave concordant results. In the remaining experiments, the fourth to the twenty-first inclusive, one gram of brushite was employed in each and the shaking period was two days.

Results and Discussion.

The data are contained in Table II. Magnesium concentrations were calculated by balancing for electrical neutrality with the experimentally determined concentrations of the other radicals present.

TABLE II.—SOLUBILITY OF BRUSHITE AT 40° C.

[Ca.]	[Total P]	[Foreign Cation.]	[Foreign Anion.]	p_H at 25° C.	μ.	p_{KSP}.
0·00241[e]	0·00500[c]	—	—	5·09	0·0077	6·27
0·00250[c]	0·00672[c]	- -	—	5·55	0·0087	6·24
0·00332[c]	0·00852[c]	—	—	5·36	0·0112	6·20
0·00252[e]	0·00490[c]	0·0400[a](Na)	0·0400[a](Cl)	5·89	0·0482	5·91
0·00311[e]	0·00550[c]	0·1000[a](Na)	0·1000[a](Cl)	5·87	0·1100	5·68
0·00388[e]	0·00645[e]	0·2000[a](Na)	0·2000[a](Cl)	5·81	0·2123	5·45
0·00516[e]	0·00772[e]	0·4000[a](Na)	0·4000[a](Cl)	5·73	0·4164	5·20
0·00641[e]	0·00908[e]	0·8000[a](Na)	0·8000[a](Cl)	5·66	0·8200	4·95
0·00711[c]	0·00992[c]	1·0000[a](Na)	1·0000[a](Cl)	5·50	1·0220	4·91
0·00401[c]	0·00826[c]	0·1000[a](K)	0·1000[a](Cl)	5·60	0·1130	5·66
0·00548[e]	0·00904[e]	0·4000[a](K)	0·4000[a](Cl)	5·67	0·4170	5·26
0·00688[e]	0·01160[e]	1·0000[a](K)	1·0000[a](Cl)	5·68	1·0220	4·97
0·00492[e]	0·00977[c]	0·0952[a](Na)	0·0472[e](SO4)	5·77	0·1580	5·29
0·00597[e]	0·01110[c]	0·1904[a](Na)	0·0945[c](SO4)	5·85	0·3050	4·98
0·00769[e]	0·01290[c]	0·3808[a](Na)	0·1900[e](SO4)	5·94	0·5970	4·63
0·00507[e]	0·00576[c]	0·0180[e](Mg)	0·0194[e](SO4)	5·82	0·0890	5·35
0·00780[c]	0·00630[c]	0·0454[c](Mg)	0·0490[e](SO4)	5·94	0·2100	4·86
0·01350[c]	0·00778[c]	0·0890[c](Mg)	0·0970[c](SO4)	6·00	0·4080	4·37
0·02280[c]	0·00524[c]	—	0·0406[a](Cl)	4·02	0·0686	5·47
0·04300[c]	0·00481[c]	—	0·0811[a](Cl)	4·77	0·1290	5·21
0·08370[e]	0·00454[c]	—	0·1623[a](Cl)	4·63	0·2510	4·94

Sodium, potassium, and chloride concentrations were assumed from their original molarities. Concentrations estimated by direct experiment are followed by the elevated symbol " e," those assumed, by " a," and those calculated, by " c." μ was obtained roughly and used with p_H and the appropriate curve in Fig. 1 to find the approximate distribution of phosphate fractions. This permitted a more accurate fixing of

both μ and [HPO$_4$]/[total P]. $p_{K_{sp}}$ was then calculated from equation (1) on the assumption that [Ca^{++}] = [Ca]. The preponderating salt in solution in the first three experiments was Ca(H$_2$PO$_4$)$_2$. In the absence of experimental data relating the variation of $p_{\overline{K}_2}$ to this salt, equation (19) was employed.

The second and third experiments show a notable deficiency of calcium associated with the phosphate in solution. Apparently freedom from chloride in the washings from brushite preparations could not be accepted as a criterion for freedom from alkali metal phosphates. In both cases the resulting error in μ is about 0·0008. The first experiment, in which, as in those remaining, only 1 gm. of solid brushite was used, shows a similar but smaller deficiency, the error in μ naturally being sensibly proportional to the amount of solid brushite. μ was corrected neither for these small errors nor for expansion of the solutions (about 0·25 per cent.) between 20° C. and 40° C.

$p_{K_{sp}}$ errors due to solution expansion, are negligible. $p_{K_{sp}}$ values were plotted against $\sqrt{\mu}$ values as shown in Fig. 2. $p_{K'_{sp}}$ was obtained by extrapolating the NaCl curve to $\sqrt{\mu} = 0$ with the help of equations (6) and (7). The other curves were considered before fixing its value at 6·56.

Equations of the form of (6) fitting three of the curves well, are :—

$$\text{KCl as foreign salt}: \quad p_{K_{sp}} = 6\cdot56 - \frac{4\cdot15\sqrt{\mu}}{1 + 1\cdot60\sqrt{\mu}} \qquad . \quad (24)$$

$$\text{NaCl as foreign salt}: \quad p_{K_{sp}} = 6\cdot56 - \frac{4\cdot15\sqrt{\mu}}{1 + 1\cdot50\sqrt{\mu}} \qquad . \quad (25)$$

$$\text{Na}_2\text{SO}_4 \text{ as foreign salt}: \quad p_{K_{sp}} = 6\cdot56 - \frac{4\cdot15\sqrt{\mu}}{1 + 0\cdot83\sqrt{\mu}} \qquad . \quad (26)$$

The CaCl$_2$ and MgSO$_4$ curves can be extrapolated to $p_{K'_{sp}} = 6\cdot56$ only by crossing the limiting straight line, and equation (5) makes no provision for this. The limits of ionic approach must be so close that the Debye-Hückel approximation, investigated by Gronwall, La Mer, and Sandved, is no longer permissible. The limiting straight line in such cases is steeper, and the curves have been shaped to agree with what the investigations further revealed.

Denominator terms in equations (20), (21), (22), (23), (24), (25) and (26), take limits of ionic approach into account only in a broad sense, and it would be futile to attempt the deduction of ionic size from them. The order of the experimental curves in Fig. 1 is not exactly preserved in Fig. 2, and the reason for this is so obscure that it is difficult to decide whether the theory could or could not account for it. In a general way, however, it might be concluded that univalent ions are larger as a rule than bivalent.

By the mass law, it may be shown for solutions of unvarying thermodynamic environment in equilibrium with pure solid brushite and Ca$_3$(PO$_4$)$_2$, that [Ca^{++}]/H^2 is constant. Whilst it cannot be claimed that any of the solutions studied in this paper were saturated with respect to Ca$_3$(PO$_4$)$_2$, and although ionic environments were not the same, it is interesting to note that the solutions containing CaCl$_2$ were of relatively low p_H.

Behrendt's [13] data on brushite solubility were not available to the present author. Those of Kugelmass and Shohl [14] were not suitable for recalculation because their solutions contained $NaHCO_3$. Holt, La Mer, and Chown [15] briefly studied the solubility of brushite at 38° C.
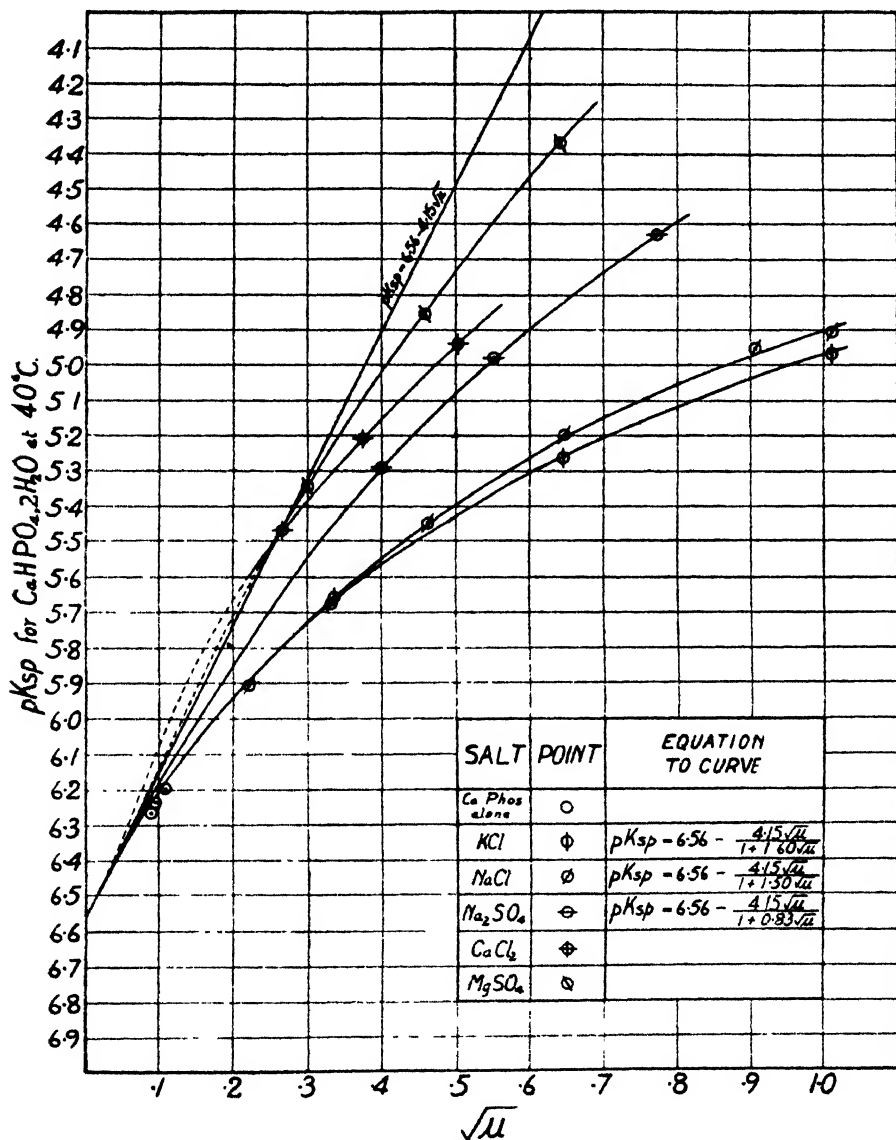
FIG. 2.

Their use of the gas electrode and a p_H standard which might not be compatible with the present author's, lead to uncertain recalculation errors. However, their data yield three points in duplicate: $\sqrt{\mu} = 0.129$,

[13] *Biochem Z.*, **146**, 318, 1924.   [14] *J. Biol. Chem.*,**58**, 649, 1924.
[15] *Ibid.*, **64**, 509 and 567, 1925.

$p_{\text{Ksp}} = 6 \cdot 10$, and $\sqrt{\mu} = 0 \cdot 127$, $p_{\text{Ksp}} = 6 \cdot 13$ (in absence of foreign salt) ; $\sqrt{\mu} = 0 \cdot 342$, $p_{\text{Ksp}} = 5 \cdot 55$, and $\sqrt{\mu} = 0 \cdot 341$, $p_{\text{Ksp}} = 5 \cdot 63$ (in presence of NaCl) ; and $\sqrt{\mu} = 0 \cdot 657$, $p_{\text{Ksp}} = 4 \cdot 32$, and $\sqrt{\mu} = 0 \cdot 657$, $p_{\text{Ksp}} = 4 \cdot 30$ (in presence of $MgSO_4$). Excepting the first of the NaCl pair, the points fall remarkably well upon the appropriate curves in Fig. 2. Domontovitsch and Sarubina [16] studied the solubility of brushite at 19-22° C. Their data have been recalculated and yield the following five points : $\sqrt{\mu} = 0 \cdot 053$, $p_{\text{Ksp}} = 6 \cdot 39$, and $\sqrt{\mu} = 0 \cdot 055$, $p_{\text{Ksp}} = 6 \cdot 35$ (in absence of foreign salt) ; $\sqrt{\mu} = 0 \cdot 235$, $p_{\text{Ksp}} = 5 \cdot 86$, and $\sqrt{\mu} = 0 \cdot 326$, $p_{\text{Ksp}} = 5 \cdot 65$ (in presence of NaCl) ; and $\sqrt{\mu} = 0 \cdot 323$, $p_{\text{Ksp}} = 5 \cdot 06$ (in presence of $CaCl_2$). The two NaCl points fall above the NaCl curve in Fig. 2 by about 0·03 in p_{Ksp}. Whilst the Debye-Hückel theory would allow a small shift in the other direction, the activity of solid brushite itself might conceivably change with temperature. The point cannot be argued from these results because the possible error in p_{Ksp} exceeds 0·03. Their single $CaCl_2$ point inexplicably falls above the $CaCl_2$ curve by more than 0·2 in p_{Ksp}.

In reviewing all the data obtained in absence of foreign salt, it is important to note that Domontovitsch and Sarubina's solutions were of high p_{H}, most of the phosphate existing as $HPO_4^=$. Specific ion effects are so small at these low concentrations that all the points should fall closely upon a straight line of theoretical slope if application of the mass law and the Debye-Hückel theory is justified. Judged from this criterion, the present treatment is entirely satisfactory.

In view of the possibly incomplete ionisation of $MgSO_4$ and the chance that incompletely ionised magnesium phosphates may exist, it is perhaps surprising that the recalculated data of Holt, La Mer, and Chown should be in such striking agreement with the data of the present study, because the determinations detailed in Table II. were made in solutions of lower p_{H}, and consequently the phosphate distributions were not the same as in Holt, La Mer, and Chown's solutions.

Summary.

1. It has been found that solid brushite ($CaHPO_4$, $2H_2O$) is stable in contact with aqueous salt solutions at 40° C. The temperature of transition of brushite to monetite ($CaHPO_4$) in the presence of a more basic salt (supposedly $Ca_3(PO_4)_2$) and in contact with salt solutions, seems to be above 40° C.

2. The second dissociation of phosphoric acid in solutions of NaCl, KCl, Na_2SO_4, $CaCl_2$, and $MgSO_4$ at 23·5° C., has been investigated, and equations connecting the dissociation with salt concentration have been deduced in the cases of NaCl, KCl, and Na_2SO_4.

3. The solubility of brushite in aqueous solutions of the same five salts and also in water at 40° C., has been investigated, the calculations requiring detailed knowledge of the second dissociation of phosphoric acid but not necessarily at that same temperature. Again in the cases of NaCl, KCl, and Na_2SO_4, it has been found possible to deduce equations connecting solubility product with salt concentration. Recalculations of pre-existing data have been made and good agreement has been obtained The solubility of brushite cannot vary much with temperature.

4. All results have been discussed in the light of the Debye-Hückel "inter-ionic attraction theory" from which the working equations have been deduced.

[16] *Biochem. Z.*, **162**, 464, 1925.

In conclusion, the author wishes to thank, among others, Dr. G. A. Elliott and Professor N. T. M. Wilsmore of the University of Western Australia, for kindly interest and criticism.   He wishes also to acknowledge his indebtedness to the Council for Scientific and Industrial Research for permission to publish the work, and to submit it as a thesis for the degree of Master of Science.

THE ELECTRO-DEPOSITION OF SILVER FROM ARGENTOCYANIDE SOLUTIONS.   PART II.

By Samuel Glasstone and Edward B. Sanigar.

In the course of experiments made on the influence of various anions on the nature of the silver deposited by the electrolysis of argentocyanide solutions (Part I.) * it was found that the presence of cyanate in the electrolysis bath had a marked effect on the deposit.   As cyanate is a possible constituent of silver-plating baths, and its influence on the deposit was found to be characteristic, it was considered advisable to make a separate report of the work.   The present paper contains an account of the results obtained.

Experimental.

The general experimental details were the same as in previous work ; [1] the stock solution contained 20·5 g./litre of silver, 85 per cent. " excess free cyanide," and was 1·5 N with respect to sodium carbonate.   The preparation of the sheet copper cathodes and the conditions of deposition were the same as in the previous study.   Depositions and cathode potential measurements, by the commutator-extrapolation method,[2] were made in a series of solutions containing, in addition to the stock constituents, from 0·05 to 1·0 g. equiv. of potassium cyanate per litre.

Deposits.—In the preliminary experiments cyanate had been added to the argentocyanide solution until the concentration of the former was 1·25 N, in order that the results might be comparable with those obtained by the addition of other anions (see Part I.) ; the silver deposited from this electrolyte showed a remarkably uniform microcrystalline structure.   The deposits were quite smooth to the touch, and were brighter than those obtained from the stock solution.

To determine the concentration at which the influence of the cyanate became operative, deposits were made from a series of argentocyanide solutions which were 1·0, 0·75, 0·50, 0·25, 0·15, 0·10, 0·075 and 0·05 N with respect to cyanate.   There was little difference between the deposits from the 0·5 N solution, and those containing larger amounts of cyanate ;

[1] Glasstone and Sanigar, Trans. Faraday Soc., 25, 590, 1929.
[2] Glasstone, Jour. Chem. Soc., 125, 250, 1924 ; 642, 1927.

hence at this concentration the anions under consideration appear to be exerting their maximum influence on the silver deposit. At concentrations as low as 0·15 N cyanate the micro-crystalline structure could be observed distinctly, whereas at still lower concentrations the deposits were inclined to be patchy. Deposits from solutions containing 0·10 N cyanate were milky (semi-bright) and smooth. This seems to represent a transition stage between the matt deposit due to the carbonate present and the crystalline structure due to the cyanate. It is thus possible to produce a smooth, semi-bright deposit of silver by the addition of cyanate to an argentocyanide bath containing carbonate, but the relative concentrations must be carefully controlled.

Although the stock solution, which contained carbonate but not cyanate, gave regular matt deposits, there was occasionally a tendency to non-uniformity; if cyanate were present in a concentration exceeding 0·1 N, however, the deposits obtained in the course of many experiments were *always* perfectly uniform. Whereas the ordinary silver-plating solutions seem to be disturbed by uncontrollable external, or possibly internal, factors, those containing cyanate repeatedly gave identical deposits. It appears, therefore, that the presence of cyanate in silver plating baths has the beneficial effect of facilitating uniformity of deposition. On standing, or on continuous use, the effect of the added cyanate decreased under the conditions of the present experiments; this may not necessarily happen, however, when the solution is agitated in contact with air, as is the case in technical silver-plating practice. Whilst the effect of the cyanate was wearing off the deposits passed through a milky (semi-bright) to a patchy stage, and finally back to the matt deposits of the stock solution.

The ease with which deposits from baths containing cyanate could be polished was tested by the hand burnishing method described in the previous paper.[1] The deposits from the stock solution were very easy to burnish, and so also were those from solutions containing 0·1 to 0·2 N cyanate; the patchy deposits obtained from solutions with a lower cyanate content were naturally more difficult to burnish. The markedly micro-crystalline deposits from 0·25 N and more concentrated cyanate solutions burnished readily, but not quite so easily as the deposits from the stock solution; this difference, no doubt due to differences in the surface structure, was confirmed by a trade plater who " finished " (*i.e.* polished with lime and rouge on mops) several of the deposits.

Anodes.—In almost all instances the silver anodes in the baths containing cyanates were remarkably crystalline and sparkling, becoming more so with continued use. They behaved in a very satisfactory manner except for a slight tarnishing, which became observable at a cyanate concentration of 0·25 N and increased somewhat with increasing cyanate content of the baths. This tarnish dissolved rapidly when the current was stopped, and did not, as far as was observed, interfere with the anodic dissolution of the silver (*cf.* effect on the anode of too little free cyanide in conjunction with high carbonate content, Part I., p. 595). This tarnish would probably not have formed, or at least not to the same extent, if the solutions had been agitated more vigorously. Since sparkling anodes are considered desirable in silver plating the addition of a *small* amount of cyanate would probably have a beneficial effect on an otherwise unsatisfactory anode.

Cathode Potentials.—The addition of potassium cyanate in concentrations up to 0·5 N produced a small, but definite, decrease in the

deposition potential of silver at the higher current densities used ; subsequent additions resulted in no appreciable further change, and so the results quoted are only for solutions up to 0·5 N in cyanate.

TABLE I.—CATHODE POTENTIALS ON THE HYDROGEN SCALE.

Current Density (amps./ sq. dm.).	Stock Solution.	Concentration of Cyanate.				
		0·05 N.	0·10 N.	0·15 N.	0·25 N.	0·50 N.
—	−0·41	−0·41	−0·41	−0·41	−0·41	−0·41
0·15	−0·51	−0·50	−0·49	−0·49	−0·47	−0·46
0·30	−0·59	−0·57	−0·54	−0·53	−0·51	−0·50
0·40	−0·69	−0·67	−0·63	−0·60	−0·56	−0·55
0·45	−0·80	−0·76	−0·73	−0·71	−0·68	−0·67

Comparing the results for the cyanate solutions with those given by the stock solution, it is clear that the presence of cyanate in an argentocyanide bath reduces the polarisation during silver deposition. The bright and semi-bright deposits obtained from such solutions are, presumably, associated with this decrease in the cathodic polarisation. It has been found that similar results are obtained when a carbon disulphide or alkali sulphide brightener is used in silver-plating solutions.[3]

Discussion.

In previous work[1] it was not possible to correlate the deposition potential of silver with the type of deposit obtained, or with the " hardness " of the deposit as estimated by ease of polishing. From the results of the present work it seems that substances which cause bright silver deposits to be given by argentocyanide solutions lower the cathodic polarisation.

It is sometimes stated as a general principle that in the electrodeposition of metals from solutions of their simple salts small crystals, and hence bright deposits, are obtained when the cathode polarisation is high.[4] The generalisation does not necessarily hold, however, for deposition from solutions of complex ions, where the metal ion concentration is extremely small. In fact, the results reported here are opposed to this general statement, since cyanates, carbon disulphide, and other sulphides actually decrease the cathodic polarisation whilst yielding bright deposits. It has already been shown[1] that the addition of cyanide to an argentocyanide solution causes a decrease in cathode polarisation, i.e. a smaller polarisation for a given current density, and a brightening of the deposit,[*] whereas the substances which increase the polarisation, e.g. carbonates, give matt deposits.

[3] Haring, *Trans. Amer. Electrochem. Soc.*, **49,** 417, 1926 ; and independent work by the present authors.
[4] *Cf.* Aten and Boerlage, *Rec. Trav. Chim.*, **39,** 720, 1920 ; Blum and Rawdon, *Trans. Amer. Electrochem. Soc.*, **44,** 397, 1923 ; see, however, Clarke and Jones, *Trans. Faraday Soc.*, **25,** 582, 1929.
[*] Aten and Boerlage (Ref. 4, p. 730) state that the polarisation for a given C.D. is smaller in a solution of a complex salt to which has been added an excess of the substance producing the complex, and that from such solutions, e.g., KAg(CN)$_2$ + KCN, deposits are more *coarsely* crystalline than from solutions of the complex salt alone. Whilst this may be true for small additions of cyanide, it does not hold when considerable amounts of free cyanide are present (Sanigar, *Trans. Faraday Soc.*, **25,** 1, 1929.)

The attainment of the maximum effect of cyanate on the polarisation at a concentration of about 0·5 N corresponds roughly with the limit above which there is no further influence on the nature of the deposit ; hence it is not improbable that there is some definite connection between the cathode potential and the appearance of the silver deposit. The fact that a commercial brightening preparation, made from carbon disulphide, decreased the cathodic polarisation to the same extent as did the addition of 0·1 to 0·15 N cyanate, but gave a bright deposit of quite a different type, shows, however, that deposition potential cannot be the only factor influencing the nature of the deposit. It seems probable, as suggested in Part I., that the preferential adsorption of addition agents on certain faces of the growing crystals may account for differences in the electro-deposits ; since unimolecular layers only are necessary, the marked effect of small amounts of certain brightening agents is readily accounted for.

Summary.

(1) The addition of potassium cyanate in concentrations greater than about 0·1 N to an argentocyanide solution containing 1·5 N carbonate results in the production of remarkably uniform micro-crystalline electro-deposits of silver.

(2) The change in the nature of the deposit resulting from the addition of cyanate is accompanied by a decrease in cathodic polarisation.

(3) Carbon disulphide and other substances, which are able to act as brightening agents in silver deposition, also lower the polarisation.

(4) It appears that a high cathodic polarisation in the deposition of silver from argentocyanide solutions favours the production of matt deposits, whereas bright deposits are obtained when polarisation is low.

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THE DECOMPOSITION OF NITROUS OXIDE AT LOW PRESSURES UPON A PLATINUM CATALYST.

BY G. VAN PRAAGH AND B. TOPLEY.

The heterogeneous reaction $N_2O = N_2 + \frac{1}{2}O_2$ has been studied with electrically heated platinum wires by Hinshelwood and Prichard [1] at pressures of the order of a few hundred millimetres ; also measurements by W. Thrun in the range 0·05 to 1·0 millimetres are reported by Cassel and Glückauf.[2] The two investigations agree in the conclusion that the reaction is of the first order with respect to nitrous oxide and is retarded by oxygen and uninfluenced by nitrogen. In both investigations smooth curves were obtained for the amount of reaction plotted against time, the rate being greatest at the beginning of the reaction.

In 1928-29 we attempted measurements of the low pressure decomposition by platinum, using the hot wire method. We found,

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[1] *J. Chem. Soc.,* **127**, 327, 1925.   [2] *Z. physik. Chem.,* **B. 9,** 427, 1930.

however, that the wire rapidly increased in activity with use and that the reaction on the activated catalyst is kinetically of quite a different character from the reaction on the unactivated wire; in general there is an induction period followed by a period of rather rapid reaction which ceases completely before all the nitrous oxide has been decomposed. The work reported here and the discussion are mainly concerned with the activated catalyst.

Experimental Arrangement.

The diagram shows the important parts of the apparatus. The reaction vessel (R.V.) (350 c.c.) is efficiently thermostated at $25° \pm ·02$.
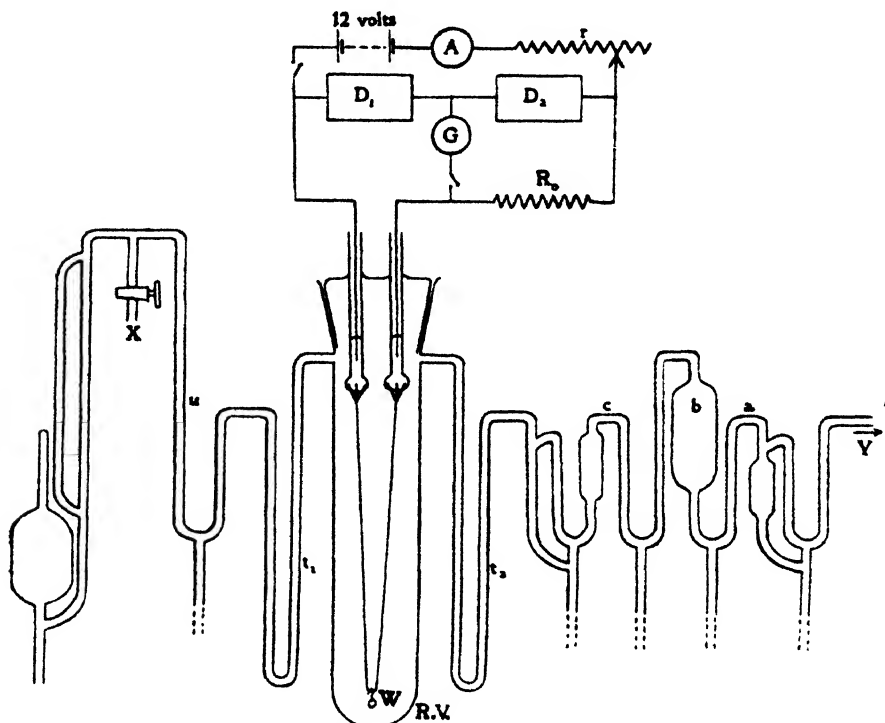
X = to pumps.
Y = storage vessel containing N_2O at 5 mm.

The catalyst wire is welded on to thick triple platinum leads capable of carrying a heavy current, sealed into the glass tubes which carry mercury connections and are themselves sealed into the ground joint. The catalyst wire (30 cm. long, 0·0315 cm. diameter) was in the form of a loop kept in position by a small silica weight W hung on by a fine silica fibre.

Nitrous oxide from a cylinder was dried and fractionally distilled three times, and stored at a few millimetres pressure. Its complete freedom from permanent gas could be tested at any time by condensing a sample in the apparatus by liquid air and measuring the residual pressure on the McLeod gauge.

Nitrous oxide entered the reaction vessel through a long and narrow U tube (t_2) coated inside with spongy gold [a] (by decomposition of the chloride) and cooled in solid carbon dioxide. The reaction vessel was connected through a second gold-filled trap (t_1) and through the cut-off (u) to the McLeod gauge and through the tap to the usual system of pumps. The two traps (t_1) and (t_2) are brought together into the same Dewar vessel just outside the thermostat.

For the purpose of introducing definite small pressures of nitrous oxide into (R.V.) the arrangement (a, b, c) of gas pipettes operated by mercury cut-offs proved very convenient. By successive expansions from a into b and from c into (R.V.) any desired pressure from 10^{-3} mm. upwards was obtained. The guard tube (c') on (c) is necessary when pressures of the order of 0·1 mm. are expanded directly from (c) into (R.V.) to return any drops of mercury splashed over by the gas expanding into the vacuum.

Measurement of the Extent of the Reaction.—After introducing the nitrous oxide, (cc') is closed and the gas pressure measured. The cut-off (u) is then closed and the McLeod gauge evacuated. After heating the wire the gauge is connected in again ; the new pressure, multiplied by the appropriate factor, gives the gas pressure in (R.V.) after reaction. This factor (1·472) was determined directly by similar pressure measurements with pure nitrous oxide in the apparatus. The McLeod gauge proved to be a satisfactory method of determining the extent of reaction with an accuracy of 1 per cent. of the original amount of nitrous oxide. Fortunately the wire itself could be used as a sensitive Pirani gauge to observe quite small changes, as described below.

The Electrical Circuit.—The Wheatstone bridge circuit used to measure the resistance and hence the temperature of the wire is included in the diagram. The heating current, drawn from six large capacity accumulators, passed through the catalyst wire and a constant resistance (R_0) in series. (R_0) consisted of a grid of twelve fine manganin wires in parallel, immersed in thin oil (stirred by an air stream) in a narrow metal tank sunk in the thermostat. The temperature coefficient of resistance of manganin is practically zero at 25° and the oil never reached 26°, so that R_0 remained perfectly constant even when carrying up to 3 ampères.

The other side of the circuit consisted of two dial resistance boxes (D_1) and (D_2) each with a range of 0 to 10,000 ohms in units. The total resistance in the two boxes was never set below 7000 ohms. The heating current was adjusted by a series of mutually shunted low resistance rheostats with a very fine adjustment, represented by (r). The ammeter (A) was only a rough guide.

Temperature Control.—The resistance of the catalyst wire varied from about 1 to 3 ohms, with (R_0) constant at 1·021 ohms. The Wheatstone bridge ratio is thus rather an unfavourable one ; nevertheless, using a Moll galvanometer the balance could be found with ease to one unit of (D_1), so that a change of 0·1° in the temperature of the wire could be detected, and in practice the temperature could be controlled to 0·2° by hand regulation of (r), when the composition of the gas in (R.V.) was not changing too quickly. With the wire as it was used in

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[a] This has the advantage that the change in appearance of the brownish gold to white, as it takes up mercury, is very distinct, and it can be seen when the trap needs renewal. A disadvantage is that to be efficient at low pressures the trap must be long and narrow, and the time of pumping is prolonged.

practice, from 500° to 1200° higher than its surroundings, this represented a very sensitive qualitative hot wire gauge, since at pressures of the order of 0·1 to 0·01 mm. there is a considerable increase in thermal conductivity when the equivalent of N_2 and $\frac{1}{2}O_2$ mixture is substituted for N_2O. This proved particularly useful as a criterion either of the fact that reaction was beginning or that it had ceased entirely.

Accuracy of the Temperature Measurement.—The platinum wire used was directly calibrated as a resistance thermometer, up to 700°, against an accurately calibrated thermocouple ; temperatures above this were estimated by extrapolation. The catalyst being rather thick necessitated a considerable end correction, and the actual Centigrade temperatures given are subject to an uncertainty in their absolute values of up to 4 per cent. It will be seen that this uncertainty is not important. But the accurate reproducibility and control of the temperature is very important, because during the induction period a rise of a few degrees would sometimes cause rapid reaction.

The Absorption and Evolution of Gas by the Wire.

In the heterogeneous reaction at low pressures the reaction once started proceeds rapidly to a limit, but the pressure increase does not then correspond to complete decomposition into nitrogen and oxygen. Since there are about 1200 platinum atoms in the wire for every oxygen atom in the nitrous oxide filling the reaction vessel at 0·1 mm. pressure, the question of solution of gas in the wire is important, although it had not been anticipated that this would be appreciable at the low pressures and high temperatures employed, or in the very short time taken by the wire to cool in the gas.

The activated wire does in fact take up considerable quantities of gas. Starting with the wire in a practically completely " de-gassed " condition, a number of decompositions were done between 500° and 700°, after which an amount of gas corresponding to a pressure of 0·09 mm. in the reaction vessel was obtained from the wire by heating it to 1500° in vacuo for several hours ; the total amount was calculated by measuring the rate of gas evolution at intervals and summing over the whole time of heating.

Any change in the gas content of the wire during a reaction can be detected by comparing the amount of nitrous oxide decomposed (a) from the pressure increase, on the assumption that two reactant molecules produce three product molecules, (b) by freezing out the unchanged nitrous oxide [*] in the lower part of the traps (t_1) and (t_2). Table I. contains the results of this comparison for five consecutive experiments taken at the end of a sequence done *without* heating the wire in vacuo between the experiments.

The second column gives the temperature at which the reaction proceeded rapidly to the limit represented by the increase in pressure shown in the fourth column. The quantities of gas recorded in the last five columns are expressed in terms of the pressure exerted in the reaction vessel alone, the unit being thousandths of a mm. of mercury. In Exp. 38 some of the reaction mixture from the previous decomposition was left in and more nitrous oxide added.

In view of other results referred to below, the agreement between (a)

[*] The vapour pressure of solid nitrous oxide was measured for this purpose, and shown to be negligible below − 175°C.   *Cf. Trans. Farad. Soc.*, **26**, 196, 1930.

and (b) is rather remarkable; it appears that after a series of reactions (prior to Exp. 35) the wire had become charged with gas, and then remained in a steady state during further experiments in the same temperature range. This, however, is merely a state of balance, since after any experiment the wire will evolve gas when heated to some higher temperature. Thus at the end of Exp. 39 the cut-off (u) was closed, leaving in the reaction vessel a mixture of known pressure and composition; then on raising the wire to a temperature 75° higher than before, more nitrous oxide was decomposed and at the same time the wire evolved a certain amount of gas, since the new value of the pressure increase exceeded the equivalent of the nitrous oxide actually decomposed.

TABLE I.

Exp.	Temperature Centigrade.	P_{N_2O} Initial mm. × 10^{-3}.	Increase after Reaction.	N_2O Decomposed (a).	N_2O Frozen Out.	N_2O Decomposed (b).
35	> 600	153·5	57·0	114·0	41·2	112·3
36	660	172·5	60·7	121·4	52·1	120·4
37	613	145·0	34·6	69·2	76·6	68·4
38	715	$\left\{ \begin{array}{c} 197 \cdot 8 \\ + 70\ N_2 + O_2 \end{array} \right\}$	58·5	117·0	82·4	115·4
39	595	145·5	21·3	42·6	103·0	42·5

On the other hand, starting with the wire in a thoroughly de-gassed state, the reverse was found: an initial 150·1 of N_2O at 754° produced 134·8 of $N_2 + O_2$ Freezing out gave 38·0 of N_2O undecomposed, so that 112·1 of N_2O have actually been decomposed, corresponding to 168·2 of $N_2 + O_2$. The difference 33·2 must have been taken up by the wire. Keeping the N_2O frozen out, the wire was heated in the products at 708°, 630°, 603° and 55°, but no further change took place in the amount of gas. This suggests that the gas is taken up during the reaction on the wire. Finally the wire was heated in vacuo at 1500° for a short time, and evolved 19 of permanent gas; the de-gassing was not carried to completion.

The Products of Reaction on the Activated Wire.

In the homogeneous decomposition it is known that although the main reaction is $2N_2O = 2N_2 + O_2$, a certain proportion of nitric oxide is produced simultaneously, perhaps by a wall reaction. A possible reaction of the platinum catalyst might be written in two stages:

$$N_2O + Pt = N_2 + Pt(O)_{adsorbed}$$
$$N_2O + Pt(O)_{adsorbed} = 2NO + Pt$$
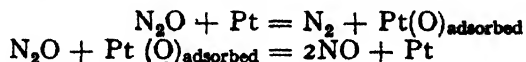
The results in Table I. provide some evidence that the low pressure decomposition on the activated catalyst is substantially into nitrogen and oxygen only. In the first place, Exps. 35-39 show that the reaction is one in which three molecules of products are produced from two of nitrous oxide. This condition is fulfilled by the decomposition into nitric oxide as formulated above. But if any considerable proportion decomposed in this way, there would be a subsequent reaction $2NO + O_2$ $= 2NO_2$ which would prevent the agreement between (a) and (b) in

Table I.   Calculation from the velocity data of Bodenstein and Linder [5] shows that the termolecular combination of nitric oxide with oxygen, although negligibly slow at the low gas concentration in the reaction vessel, would become measurable though still slow in the mixture compressed in the capillary tube of the McLeod gauge.   No such effect was observed, and it is probable that any nitric oxide produced is less than 1·5 per cent. of the nitrogen produced.

The Progressive Activation of the Catalyst.

The first eleven [6] experiments done with the wire are summarised in Table II.   It is clear that the wire increases in activity.

TABLE II.

Exp.	P_{N_2O} mm. × 10⁻³.	Per Cent. Decomposed per Minute.	Remarks.	Temperature Centigrade.
1	224	5	S	1100–1200
2	90–100	4	C. Gas let in to heated wire.	1177
3	143	5	N	1177
4	111	Nil.	S	764
5	111	9	N	1084
6	213	0·7	S	891
7	121	21	C	1204
8	108	15	N	1210
9	205	22	N	1122
10	61	28	N	1192
11	123	Nil.	S	566
		0·4	N	847
		7·5	N	935

The letters in the fourth column refer to the treatment of the wire before the experiment.   C = considerably " de-gassed," S = slightly " de-gassed," N = not heated in vacuo.

In Exps. 1, 2, and 3 the reaction proceeded smoothly and without any induction period, at 1100° to 1200°; in Exp. 5 the rate was greater at 1084° than previously at 1177°; in Exp. 6 the rate is perceptible at 891°.   Exps. 7, 8, 9 and 10 show considerably greater rates than Exps. 1, 2 and 3.   In Exp. 11 the rate is perceptible at 847°, and is faster at 935° than originally at 1177°.

When the reaction was allowed to continue until the rate became quite small (at 1100° to 1200°) the pressure increase was consistent with what was roughly calculated as corresponding to 100 per cent. decomposition.

The general nature of the reaction in the first six of these runs was qualitatively similar to the results given in detail by Cassel and Glückauf, and is in marked contrast with the behaviour observed in later runs with the activated wire.   Cassel and Glückauf do not refer to any activation effect, and quite possibly the activity of the wire which they

[5] *Z. physik. Chem.*, **100**, 87, 1922.
[6] In these, pressure measurements were made with the connection (*u*) to the McLeod Gauge left open during the reaction, originally with the object of finding limits of temperature within which rate measurements could be made ; the rates obtained are therefore only rough values.

used remained sensibly constant through the six experiments for which they give detailed results. Hinshelwood and Prichard give direct proof that no drift in the activity of their wire occurred during the research.

No clear connection could be traced between the extent of the previous heating of the wire in vacuo at 1500° and its activity in the experiment which followed.

Catalysis by the Wire in the Fully Activated State.

The activity of the wire increased rapidly after Exp. 11, finally reaching a maximum. In this state the characteristic feature of the heterogeneous reaction became a period of induction or hesitant reaction, followed by rather rapid reaction. The temperature range in which this occurred was now as low as 500° to 700°.

The method of experiment was to enclose a measured pressure of nitrous oxide in (R.V.) between (u) and (cc') and to raise the wire temperature by stages until the wire showed a tendency to decrease in resistance, indicating (by its function as a hot wire gauge) that reaction was beginning. By recording the alteration with time of the fine adjustment of r required to maintain the temperature of the wire constant, a rough indication of the progress of the reaction was obtained. The final extent of reaction was measured exactly by connecting through to the evacuated gauge, as already described.

The following description is typical of thirty-two experiments done with the activated wire : there is no measurable reaction at all until some temperature in the range 490° to 720° is reached. A slow reaction begins which either rapidly accelerates, or ceases completely after a small fraction (up to about 5 per cent.) of the gas has decomposed. In the latter case a further increase of temperature—sometimes as little as 10°—again causes a slow reaction which either accelerates or stops. In some experiments this was repeated at several temperatures, but in almost every case the final result was a period of rapid reaction lasting from 2 to 10 minutes, which then ceased rather abruptly. It has been shown already (Table I.) that after this stage the nitrous oxide is by no means completely decomposed.

An actual induction period was sometimes observed, the extreme example being in Exp. 17 : after " de-gassing " the wire in vacuo at 1500° for five minutes, 94·8 . 10^{-3} mm. of nitrous oxide was introduced, and the wire was heated to 624° ; the temperature remained constant for seven minutes, indicating that no reaction exceeding 0·25 per cent. occurred in this time, and then suddenly started falling. The temperature was regulated to remain as nearly as possible constant, but the reaction ceased entirely after three minutes. The pressure increase was then found to be 18·2 . 10^{-3} mm., corresponding to 36·4 per cent. decomposition.

The temperature at which rapid decomposition set in varied considerably from one experiment to the next, as also did the final amount of reaction. The latter might in part be only apparent, because of change in the gas content of the wire, but cannot be ascribed mainly to this, as the data in Table I. show. We attempted to find a connection between the antecedent treatment of the wire and its activity as measured by the temperature at which it would induce considerable decomposition, but the results show that the time of heating at 1500° in vacuo is not very important, the catalyst being on the whole more active when this was not done.

Table III. is a condensed summary of the experiments in the order in which they were done; some only are recorded, the others being similar. In a few cases the rapid reaction started at once on heating the wire, but this was clearly because the temperature at which the characteristic behaviour would have been observed was overstepped.

TABLE III.

Column 1. Number of experiment.
,, 2. Pressure of N_2O in mm. $\times$ 10^{-3}.
,, 3. Temperature (°C.) at which " incipient " reaction occurred ; brackets ( ) = wire heated at that temperature for some minutes without detectable reaction.
,, 4. Temperature at which rapid reaction took place.
* = preceded by a definite induction period at this temperature.
** = period of the rapid reaction exceeded ten minutes.
,, 5. Total per cent. N_2O decomposed after the rapid reaction had ceased ; calculated from pressure increase.
,, 6. Relative extent to which catalyst had been heated in vacuo immediately before the run :—
C = considerably.
S = slightly.
N = not heated.

1.	2.	3.	4.	5.	6.
15	102	(629) ; 689	765*	80	S
17	94·8	—	624**	38	S
22	91·2	624	—	1·7	C
23	97	624	—	3·0	C
24	93·8	—	624	46	N
25A	159·5	(593)	—	0	C
26	138·2	(600) ; 666	670	40	N
27	155	—	651*, **	80	C
28	167·5	638 ; (671)	713	14·5	C
29	161	—	638	48	N
30	157·5	434	465**	38	N
31	158·5	450 ; 496	506	52	N
32	158 + 1 products	453 ; 473	501	33	N
33	156·5 + 13 products	—	470*, **	27·5	N
34	163	(468) ; 506 ; 536 ; 575	615*	50	N
38	197·8 70 products	495 ; (512) ; 537 ; 578 616 ; 660	715	59·2	N
39	145·1	451 ; 464	595	29·3	N
40	150·1	(548) ; (569) ; 602 , 674	754	61·8	C

Comparison of the reaction temperatures in Exps. 1 to 11 (Table I.) with those in Table III. shows how much the activity of the wire increased with use.

The negative result of Exp. 25A is significant ; the wire was heated in the nitrous oxide for 136 minutes without any sign of a gradual reaction ; yet in Exp. 24, at a temperature only 31° higher, rapid reaction took place over a period of six minutes, and in Exp. 30 rapid reaction was observed at a temperature 128° lower.

Discussion.

The general character of the reaction naturally at first suggested that some impurity was finding its way on to the cold catalyst wire between one run and the next and acting as a catalyst poison until it had either distilled off or had been oxidised away. The only probable sources of such impurity seemed to be (a) mercury vapour penetrating into the reaction vessel during the evacuation in spite of the gold traps ; (b) hydrocarbon vapour from the rubber-vaseline lubricant of the ground joint on the reaction vessel.

To test this point a special experiment (No. 42) was made as follows : the water thermostat round the reaction vessel was removed and replaced by a bath of solid carbon dioxide ; the gold-filled traps were surrounded by liquid air. The wire was then heated for an hour to 400° whilst a pressure lower than 2×10^{-5} mm. was maintained. Under these conditions any impurity which might have reached the wire through the gas phase should distil off on to the surrounding glass. The liquid air was then replaced by solid carbon dioxide, and nitrous oxide admitted. The catalytic action was now just as before : no reaction at 484° for some minutes ; at 570° a slow reaction which suddenly accelerated and ceased again after three minutes, when about 30 per cent. had decomposed.

It might be considered a possibility that a hydrocarbon impurity would decompose on the activated platinum instead of evaporating, so leaving some non-volatile catalyst poison which would then have to be oxidised by the nitrous oxide. But this is not consistent with the fact that the reaction so often takes place to the extent of 1 or 2 per cent., and then ceases until the temperature is raised again.

Taking into account also the fact that the general trend was towards a state of greater activity, especially in a sequence of runs in which the wire was not heated in vacuo intermediately, these considerations are strongly against attributing the characteristic feature of the reaction to accidental catalyst poisoning.

Making the supposition that adsorbed oxygen atoms play an important part in the reaction on the activated wire, we are lead to a suggestion as to the way in which the platinum causes the decomposition : as Hinshelwood and Prichard have emphasised, the principal function of the metal in this heterogeneous reaction is probably to act as an energetically efficient acceptor for the oxygen atom split off from the N_2O molecule. Recent thermal data are :

$$2N_2O = 2N_2 + O_2 + 43 \text{ Cal. ;} \quad O_2 = O + O - 117 \text{ Cal.}$$
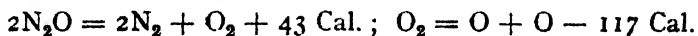
hence
$$N_2O = N_2 + O - 37 \text{ Cal.}$$
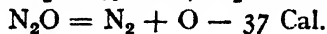
Langmuir [7] has shown that a platinum surface holds oxygen atoms tenaciously even at 1200° ; it follows that the heat of adsorption of oxygen atoms must be large, and that the reaction :

$$N_2O + Pt = N_2 + Pt(O)_{\text{adsorbed}} + X \text{ Cal.} \qquad . \qquad . \quad (1)$$

may be even exothermic. We assume that this strong adsorption applies to the " activated " metal also.

Another consequence, however, of this strong adsorption is that we cannot suppose that oxygen atoms evaporate into the gas phase

[7] *Trans. Farad. Soc.*, **17**, 621, 1921.

during the reaction, either individually or as molecules (at temperatures below 1000°). We assume therefore that reaction (1) is followed by :

$$Pt(O)_{adsorbed} + N_2O = Pt + N_2 + O_2 + Y \text{ Cal} \quad . \quad . \quad (2)$$
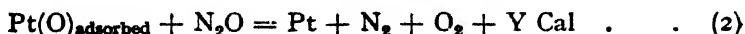
where $X + Y = 43$ Cal.

We wish now to explain the peculiar feature of the reaction—that it either takes place rapidly or not at all, and has no simple relationship between velocity and temperature (*cf.* especially Exp. 25a). This abrupt and irregular behaviour manifests itself only after the wire has undergone activation—presumably a breaking up of the original surface. Normally the molecular kinetic energy set free on a smooth metallic surface during the catalysis of an exothermic reaction will be dissipated almost immediately amongst many neighbouring metal atoms; but this is not necessarily so when, as here, the physical structure of the surface is one to which H. S. Taylor's picture of extra-lattice groups of atoms is particularly applicable. Our suggestion is therefore that some sort of " energy chain " analogous to Christiansen's original suggestion for homgeneous reactions takes place in the surface, where the complex $Pt(O)_{adsorbed}$ is alternately formed and decomposed according to equations (1) and (2). The whole reaction is made up of a number of such energy chains each localised at its own extra lattice group of atoms, which is bombarded by fresh N_2O molecules from the gas phase. As long as each " chain " continues, the mean kinetic energy associated with the group of platinum atoms corresponds to a temperature much higher than that of the system as a whole.

One possibility is represented by the scheme :

$$\begin{aligned}
&\longrightarrow Pt + N_2O = Pt^*(O)_{adsorbed} + N_2 \\
&\longrightarrow Pt^*(O)_{adsorbed} + N_2O = Pt^* + N_2 + O_2 \\
&\quad Pt^* + Pt(O)_{adsorbed} = Pt^*(O)_{adsorbed} + Pt^*
\end{aligned}$$
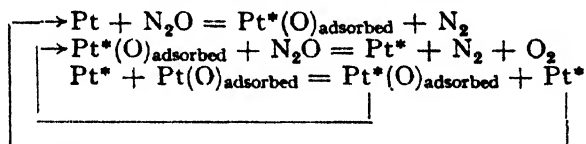
The asterisks signify that the atom or complex has temporarily an abnormally high vibrational energy.

This scheme has the following advantage : the observation of the induction period, and especially the evidence of Exp. 25a, show that reaction (2) does not proceed without a considerable activation energy, otherwise decomposition would always take place, since adsorbed oxygen atoms will always be present. The suggested energy chain provides for this.

In a reaction of this kind there will be a very sharp lower limit to the rate of the reaction localised at any one group of extra-lattice atoms ; but this extreme sharpness will not necessarily appear in the reaction velocity measured, which is the sum of the contributions from many groups of catalyst atoms, which may differ in the rate at which they lose excess vibrational energy to the underlying solid. But the influence of temperature will be very great in the region where the reaction is taking place at all, and the *measurable* reaction will begin suddenly. (*Cp.* in particular Exps. 26 and 31.)

The incompleteness of the rapid reaction is intelligible : the experimental procedure being to raise the temperature by stages until reaction started, conditions would often be obtained under which the chain mode of reaction was just possible, but a slight change in these conditions (consequent upon the reaction itself) might suffice to decrease the rate below the lower critical limit. Depending upon the uniformity or

otherwise of the groups of catalyst atoms in the metal surface, the conditions for a finite total rate will be more or less sharply defined ; whether the decomposition ceases at 1 or 2 per cent. or up to 80 per cent. will be decided by a complex set of circumstances in which the temperature of the wire, the initial oxygen content of the activated surface, the rate of diffusion of oxygen from the surface into the body of the metal, and the relative and absolute pressures and the thermal conductivity in the gas phase may all play a part. Hence the hypothesis enables us to understand what happens in this reaction, but not to predict it.

It is an interesting speculation that the enormous increase in catalytic activity which occurs with some metallic surfaces is due not so much to the increased area as to the surface becoming capable of maintaining localised energy chains in the case of exothermic reactions.

The rapid activation of the wire during the earlier experiments is interesting because the equally exothermic reaction $2CO + O_2 = 2CO_2$ on a similar platinum catalyst does not activate the surface to anything like the same extent. The difference is that as Langmuir has shown, the platinum remains covered with a layer of adsorbed CO molecules, any oxygen atoms being removed immediately as CO_2. Rideal and Wansborough-Jones [8] studying the attack of oxygen at low pressures and high temperatures, have concluded that a surface reaction is possible which breaks the binding between the platinum atoms in the surface and those lying underneath. This reaction was associated with a very high critical increment. By analogy the cause of the catalyst activation observed by us may be that the decomposing N_2O molecule provides both the oxygen atom and the excess energy to enable it to overcome the lattice forces and break up the surface ; because of the much lower temperature of our wire, the loosened platinum atoms remain on the surface as extra-lattice atoms or small aggregates of ·atoms, instead of vaporising off.

[8] *Proc. Roy. Soc.*, A. **123**, 1929.

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THE HEAT OF ADSORPTION OF HYDROGEN AND CARBON MONOXIDE ON ZINC AND CHROMIUM OXIDE CATALYSTS.

By W. E. Garner and F. E. T. Kingman.

The molar heats of adsorption of a gas on a solid surface are in general highest for the first small admissions of gas to the bare surface.[1] This is commonly ascribed to the adsorption of the gas by atoms or molecules of the adsorbent, which possess very high energy contents. These large heats of adsorption, ranging in value from 30 to several hundred Cal. are un-

[1] *Cf.* Bull, Garner, and Hall, *J. Chem. Soc.*, 837, 1931.

doubtedly associated with very marked changes in the structure of the adsorbed gaseous molecules. These changes are frequently of such a radical character as to result in the formation of new complexes of a chemical nature on the surface, as in the case of the adsorption of oxygen by tungsten,[2] and of oxygen by carbon.[3] In such cases, the process of adsorption is irreversible. More frequently, however, the changes are less intensive, as in the adsorption of hydrogen or carbon monoxide by oxide catalysts at low temperatures, and possibly also in the adsorption of hydrogen on metallic catalysts.[4] In such cases, the molecules of adsorbed gas, if not dissociated into atoms, must be highly polarised, and therefore contain greater internal energy than that of the average molecule in the gaseous state.

The relationship between the heat of adsorption and the reactivity of the adsorbed gas is likely to be very complex, not only when irreversible chemical change takes place between the surface atoms and the adsorbed gas molecules, but also when the process of adsorption is reversible. The energy of the surface atoms is not entirely set free as heat, but is partly stored in the adsorbed molecules as energy of polarisation, and it is the latter, which must contribute to the activation of the adsorbed molecules. It is unlikely that there will be found to be any quantitative relationship between the heat of adsorption and the energy of polarisation of the adsorbed molecules. There may, however, exist a qualitative correspondence between the two energies. Both the heat of adsorption, and the energy of polarisation would be expected to be greatest when adsorption occurs on the most active parts of the surface. Thus, measurements of the heat liberated on adsorption should afford some clue as to the relative magnitude of the degree of activation of the adsorbed molecules.

The activity of mixtures of ZnO—Cr_2O_3 in the methanol synthesis is greater than that of the two constituents taken separately. According to Natta,[5] who has made a special study of the structures of zinc oxide catalysts, the addition of chromium oxide or aluminium oxide to zinc oxide reduces the rate of growth of the zinc oxide granules, and thereby retards the natural decrease in the surface of the catalyst, that is, sintering, which occurs above 400-500° C. These oxides do not appear to go into solid solution in the zinc oxide lattice as is the case for copper, cobalt, manganese, iron, magnesium, and nickel oxides. They therefore do not increase the activity of the surface atoms of the catalyst by producing distortion of the lattice. The increase in catalytic efficiency which arises on mixing the two oxides would therefore appear to be due to an increase in the internal area of the oxide, and in its adsorptive capacity, and not to any change in the surface energy of the atoms. If this be correct, then no great differences should be found between the heats of adsorption of hydrogen and carbon monoxide on zinc oxide, chromium oxide, and the mixed catalyst.

Heats of Adsorption.

Employing the vacuum calorimeter described previously,[6] the heats of adsorption of hydrogen and carbon monoxide on the above catalysts have

[2] Kingdon, *Physical Rev.*, **24**, 510, 1924.
[3] Blench and Garner, *J. Chem. Soc.*, **125**, 1288, 1924.
[4] *Cf.* H. S. Taylor, *J.A.C.S.*, **53**, 578, 1931, where a summary of heats of adsorption is given.
[5] *Giorn. Chim. Ind. e. Appl.*, **12**, 13, 1930.
[6] Blench and Garner, *loc. cit.* ; McKie, *J. Chem. Soc.*, 2870, 1928.

been measured. The results are tabulated below (Table I.). These give the limiting values for the differential heats of adsorption.

TABLE I.

Catalyst.	Heats of Adsorption (Cal./mol.).	
	Hydrogen.	Carbon Monoxide.
Zinc oxide . .	—	22 → 18
Chromium oxide .	—	8 → 11
Zinc Oxide } Chromium oxide }	20 → 10	24 → 14

The adsorption of hydrogen by zinc oxide and chromium oxide catalysts was found to be very small, and accurate values for the heats of adsorption could not be obtained. The heat of adsorption of carbon monoxide on the mixed catalyst is practically the same as that for zinc oxide, although greater than that for chromium oxide. The fraction of the adsorbed gas which can be removed from the surface by evacuation at room temperature is also the same for the two zinc oxide catalysts (Table VII.). This similarity in the behaviour of ZnO and ZnO . Cr_2O_3 towards carbon monoxide indicates that this gas is adsorbed mainly on zinc oxide molecules.

The results in Table I. which give the heats of adsorption on the mixed oxide catalysts after oxidation at 300° C. are different from those reported by Kistiakowski and Flosdorf.[7] These authors find values of the order of 60 Cal. for the adsorption of hydrogen on the freshly prepared oxidised catalyst. They also note that the hydrogen could not be recovered as such on evacuation at room temperature, but was evolved as water on heating to a higher temperature. They obtained values similar to ours, 20 – 10 Cal. when the catalyst had been reduced at 300° with hydrogen. In the latter case, the hydrogen could be removed as such at 400° C.

In the case of our zinc oxide-chromium oxide catalyst, the hydrogen adsorbed on the oxidised catalyst at 25° was evolved on raising the temperature to 100° C., but was readsorbed at this temperature within a few hours. It could then be removed only as water at temperatures above 400° C. Thus, the mixed oxide catalyst used in this research is probably of an order of activity intermediate between the oxidised and reduced catalysts of Kistiakowski and Flosdorf.

No maxima were obtained on the differential heats of adsorption curves and this is also a point of difference between our results and those of the above workers. The maxima obtained by Kistiakowski and Flosdorf are very probably due to a combination of "gas" and "skin" effects (see later).

Adsorptive Capacity of the Catalysts.

The internal area of catalytic substances will depend very largely on their mode of preparation and activation, so that it is difficult to make generalisations with regard to the adsorptive capacity of a catalyst. H. S. Taylor and Kistiakowski[8] have studied the adsorptive capacities of

[7] *J. physical Chem.*, 34, 1907, 1930.   [8] *J.A.C.S.*, 49, 2468, 1927.

zinc oxide, and zinc oxide-chromium oxide catalysts. They activated their catalysts by heating to 400° C. and found that the mixed catalyst gave a much greater active area than the zinc oxide catalyst. This is true also

TABLE II.—ADSORPTION ISOTHERMS ON ZnO—CR₂O₃ CATALYST A.

Carbon Monoxide.		Hydrogen.	
c.c. Adsorbed.	Pressure (cm.).	c.c. Adsorbed.	Pressure (cm.).
0·0230	0·000045	0·0657	0·00853
0·0712	0·000502	0·1281	0·0400
0·1238	0·00159	0·230	0·1003
0·1832	0·00302	0·428	0·237
0·2387	0·00516	0·484	0·289
0·2928	0·00882	0·617	0·338

of our catalysts which were activated at 450°. They also find that zinc oxide adsorbs carbon monoxide more strongly than hydrogen. This result is also in agreement with ours. A point of difference arises, however, with regard to the relative adsorptive capacities of carbon monoxide and hydrogen on the mixed catalyst. Taylor and Kistiakowski find that the mixed catalyst adsorbs hydrogen more strongly than carbon monoxide. This is contrary to our results (Table II.). Such differences in detail would, however, be expected. Chromium oxide adsorbs very little hydrogen, but is a very much more powerful adsorbent for carbon monoxide than the mixed catalyst.

The results of this investigation support the conclusions of Natta[6] with regard to the action of chromium oxide as a promoter, *viz.*, that the increased efficiency of the mixed catalyst is due to an increase in the internal area of the catalytic surface. No modification of the heat of adsorption of carbon monoxide on zinc oxide is brought about by the addition of chromium oxide, and consequently, there is no evidence that the adsorbed molecules are more highly polarised on the mixed catalyst than on zinc oxide.

Experimental.

The technique used in this research has been described in previous papers. Certain modifications have, however, been made. The calibrated thermocouple A (Fig. 1), which entered the reaction vessel at Z.Z., was made of copper-constantin. It was connected to a Moll galvanometer which gave a deflection at a distance 2 metres of 16 cm. for 1° rise in temperature of the thermocouple. The deflections were recorded photographically. In order to make full use of this sensitivity, it was necessary to maintain the cold junctions in a thermostat constant to 0·003°, and
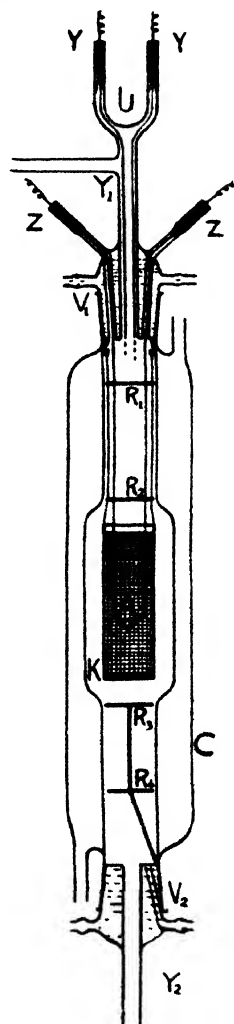
FIG. 1.

to place the switch connecting the thermocouple to the galvanometer in an oil bath.

The catalyst was contained in the platinum gauze vessel K which was suspended by means of thin platinum wire in the double-walled vessel C. Water at constant temperature could be circulated through C and the hollow stoppers V_1 and V_2. The gas was admitted as described previously. A typical record of the rise in temperature on admitting the gas is shown in Fig. 2.

FIG. 2.

In order to remove "gas effects"* the vessel (Fig. 1) and the furnace surrounding it were enclosed in an air thermostat maintained at 20° or 25° C. To test if the "gas effect" had been eliminated, helium was introduced before each series of experiments.

FIG. 3.

The pressures of the gas in contact with the catalyst were measured by means of a McLeod gauge and also by a modified form of the Rohn gauge. In the latter, a Moll single junction vacuum thermo-element A was employed in place of the larger thermopile used by Rohn [9] (Fig. 3). This was fused on to the apparatus at R and the thermopile illuminated through the fluorite lens G and window F by the radiation from a 4 v. 12 watt lamp. The e.m.f. of the thermocouple, which varied with the gas pressure, was established at the equilibrium value within a few seconds. The e.m.f. was measured by means of a Moll galvanometer. Typical curves of the galvanometer deflections, plotted against log P, are given in Fig. 4 for pressures ranging between 10^{-1} to 10^{-5} cm. for carbon monoxide and hydrogen. With the Rohn gauge it was possible to follow very rapidly the changes in pressure which occurred during the adsorption of the gas, and for this purpose, the Rohn gauge is much superior to the Pirani gauge. The rates of adsorption were much slower than the rate of adsorption of oxygen by carbon. On account of the slow rate of adsorption, the gas penetrates the whole mass of the catalyst instead of being adsorbed on the outside layers as was found by Bull, Garner and Hall (loc. cit.) for the adsorption of oxygen on carbon. It was, therefore, possible to use the platinum gauze container without introducing an appreciable error.

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* The " gas effects " are due to the occurrence of small temperature gradients within the reaction vessel, which are modified on variation in the gas pressure.

[9] Z. Elektrochem., 20, 539, 1914.

Catalysts.

Zinc Oxide.—This was prepared by precipitating zinc hydroxide from a 40 per cent. $ZnSO_4$ solution by 880 ammonia in the cold; only a slight excess of ammonia was used. The precipitate was well washed with distilled water, filtered and ignited at 450° C. It was then broken up and sieved free from dust.
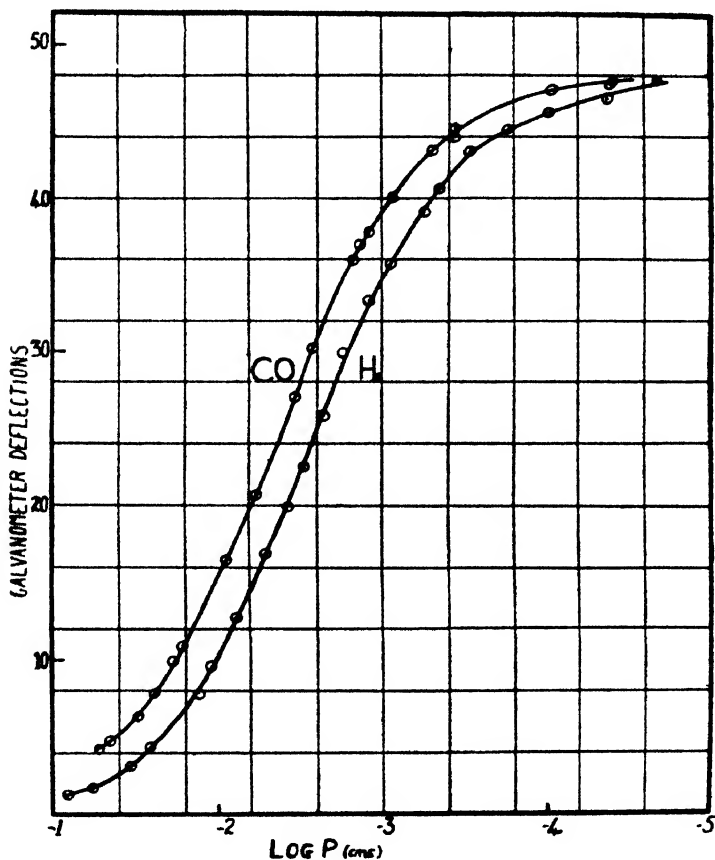
Fig. 4.

Chromium Oxide.—A 20 per cent. solution of sodium chromate, acidified with sulphuric acid, was reduced by sulphur dioxide. A slight excess of 880 ammonia was added and the solution boiled. This was treated further as in the case of zinc oxide.

Zinc Oxide—Chromium Oxide—Catalyst A.—This was prepared by precipitating a basic zinc chromate from a slightly ammoniacal solution of potassium chromate (7 per cent.) by a solution of zinc sulphate (12 per cent.). The precipitate was digested with hot water and filtered. When free from soluble salts, it was ignited at 450° C.

Catalyst B.—This was made from a 40 per cent. zinc sulphate solution and a 30 per cent. sodium chromate solution.[10] This catalyst was that mainly used in the following experiments.

[10] *Cf.* Gröger, *Monat. Chem.*, **25**, 520, 1904.

Experimental Procedure.

The catalyst was heated before each series in a high vacuum for at least two hours at 450° to remove water and carbon dioxide from the surface. After the catalyst had attained constant temperature, a small volume of helium was admitted to make sure that there was no "gas effect." This was pumped off, and a small measured volume of either carbon monoxide or hydrogen admitted. The rise in temperature of the catalyst and the rate of adsorption of gas were simultaneously measured. The rise in temperature was corrected for cooling which in these experiments was not very large.

Specific Heats.—The following specific heats were employed in the determination of the water equivalent. $Pt = 0.0314$; $SiO_2 = 0.22$; $ZnO = 0.1230$; $Cr_2O_3 = 0.1800$; Catalyst B $= 0.1151$ (determined in this laboratory by Dr. A. M. King).

Results.

Zinc Oxide.

The adsorptive capacity of this zinc oxide catalyst for hydrogen was so small that it was found impossible to make accurate determinations, and so figures for the adsorption of carbon monoxide only are given.

TABLE III.—ZINC OXIDE.

Temperature of experiment $= 25°$ C ; Weight of catalyst $= 5.016$ gm.

Expt. No.	Vol. Admitted. c.c.	Vol. Adsorbed. c.c.	Rise in Temp. °C.	Heat. (Cal.).	Total Adsorbed. (c.c.).
M 10	3.763	0.258	0.241	18.6	0.258
M 12 i	1.115	0.188	0.191	20.2	0.188
ii	5.677	0.13	0.128	20	0.32
M 14 i	0.627	0.102	0.145	22	0.102
ii	2.161	0.076	0.068	18	0.178
iii	4.393	0.049	0.050	20	0.227

The results show that the heat of adsorption of carbon monoxide on zinc oxide has a constant value of 20 Cal., and it is noteworthy that although the adsorptive capacity of this catalyst is markedly inferior to that of the mixed oxide, there is no difference between the magnitude of the heats observed in the two cases.

Chromium Oxide.

Like the zinc oxide catalyst, this catalyst had an extremely low adsorptive capacity for hydrogen. Its adsorptive capacity for carbon monoxide, on the other hand, was exceptionally high.

In the preliminary experiments with the adsorption of carbon monoxide on this catalyst, it was found that it took a very long time for the catalyst to attain the maximum temperature after adsorption of gas had taken place. In the experiments recorded below, this period was materially reduced by admitting about 0.5 c.c. of helium to the reaction vessel, before the admissions of carbon monoxide were made. The equilibrium pressures, and hence the volume of gas left unadsorbed, were calculated from a previous experiment, where no helium had been admitted. The amount of gas left unadsorbed was so small with this catalyst, that no appreciable error

was caused by this assumption. The adsorption isotherm for carbon monoxide on this catalyst is given below.

The differential heats of adsorption rise throughout a series from 8 to 11 Cal. This increase is most probably connected with the slow rate at which heat is liberated; this makes accurate measurements difficult (Table V.).

TABLE IV.—CARBON MONOXIDE ON CHROMIUM OXIDE.

Expt. N 5.

Vol. Admitted. c.c.	Equilibrium Pressure. cm.	Volume Left. c.c.	Total Volume Adsorbed. c.c.
0·3089	0·000018	0·00021	0·3087
0·3402	0·000020	0·00024	0·6487
0·4653	0·000022	0·00026	1·114
0·9269	0·000030	0·00037	2·040
1·095	0·000038	0·00046	3·135
1·653	0·000052	0·00079	4·787
1·904	0·0000885	0·00107	6·690
1·914	0·000131	0·00158	8·602
1·797	0·000266	0·00322	10·396
1·901	0·000706	0·00854	12·288
1·862	0·00244	0·02980	14·12
1·923	0·006576	0·0795	15·96

The adsorptive capacity of this catalyst is well shown by the fact that in the above table, when 10·40 c.c. of carbon monoxide have been admitted altogether, only 0·003 c.c. are left unadsorbed.

TABLE V.—CARBON MONOXIDE ON CHROMIUM OXIDE CATALYST.

Weight of catalyst = 16·707 gm. Temperature of experiment = 25° C.

Expt. No.	Vol. Admitted. c.c.	Vol. Adsorbed. c.c.	Rise in Temp. °C.	Heat. (Cal.).	Total Adsorbed. c.c.
N 5. a	0·799	0·799	0·084	7·85	0·799
b	0·330	0·330	0·0375	8·5	1·129
c	0·477	0·476	0·052	8·2	1·605
d	0·612	0·612	0·0735	8·8	2·217
e	0·698	0·697	0·080	8·6	2·914
f	1·282	1·282	0·147	8·6	4·196
g	0·641	0·641	0·069	8·1	4·837
h	0·945	0·944	0·121	9·6	5·781
k	1·959	1·958	0·304	11·6	7·739
N 9. a	0·759	0·759	0·084	8·3	0·759
b	0·771	0·771	0·0875	8·5	1·530
c	0·800	0·800	0·091	8·5	2·330
d	0·826	0·826	0·0955	8·7	3·156
e	0·819	0·819	0·096	8·8	3·975
f	0·897	0·896	0·094	7·9	4·871
g	0·868	0·866	0·106	9·1	5·737
h	0·897	0·896	0·115	9·6	6·633
i	0·864	0·863	0·104	9·05	7·496
j	0·951	0·949	0·134	10·6	8·445
k	0·929	0·926	0·124	10·0	9·371
l	1·023	1·020	0·149	11·0	10·391

Zinc Oxide—Chromium Oxide Catalyst B. Tables VI. and VII.

TABLE VI.—CARBON MONOXIDE.

Temperature of activation = 450° C.   Weight of catalyst = 12·44 gm.

Expt. No.	Vol. Admitted. c.c.	Vol. Adsorbed. c.c.	Rise in Temp. °C,	Heat. Cal./Mol.	Total Adsorbed. c.c.
Temperature of experiment = 20° C.					
H 6. i	0·0579	0·0478	0·0245	20	—
ii	0·08	—	—	—	—
iii	0·8368	0·245	0·088	14	0·338
H 8. i	0·0548	0·0479	0·019	15	0
ii	0·0744	0·0371	0·017	17	0·0902
H 10. i	0·0496	0·0468	0·036	29·5	0·0490
ii	0·0552	0·0481	0·0225	18	0·0993
iii	0·0733	0·0458	0·016	13·5	0·1536
iv	0·1514	0·0703	0·027	15	0·2522
v	0·8867	0·2652	0·102	14·7	0·5174
Temperature of experiment = 25° C.					
K 6. i	0·1917	0·1118	0·0515	17·5	0·1157
ii	0·4525	0·1005	0·0405	15·5	0·2238
iii	1·1646	0·1836	0·056	11·6	0·4074

TABLE VII.—HYDROGEN.

Expt. No.	Vol. Admitted. c.c.	Vol. Adsorbed. c.c.	Rise in Temp. °C.	Heat.	Total Adsorbed. c.c.
Temperature of experiment = 20·0° C.					
H 3. i	0·0574	0·0530	0·0215	15	0·0562
ii	0·1735	0·0579	0·024	16	0·1963
iii	0·8666	0·1337	0·0465	13	0·330
H 14. i	0·3181	0·1467	0·0845	20	0·2792
ii	0·8610	0·2544	0·067	10	0·5336
Temperature of experiment = 25° C.					
K 2. i	0·0527	0·0519	0·024	17·5	0·0524
ii	0·0783	0·0654	0·025	15	0·1284
iii	0·1702	0·0813	0·034	12·5	0·2629
iv	0·8541	0·1798	0·085	14	0·4427
K 4. i	0·0503	0·0480	0·019	15	0·0498
ii	0·0693	0·0505	0·022	16	0·1004

Desorption of Gas at Room Temperatures.

If the adsorption of gas on the oxide catalysts were completely reversible, it should be possible to remove practically the whole of the gas adsorbed at room temperatures merely by evacuating the catalyst at that temperature.

This desorption would be accompanied by an adsorption of heat equal to that evolved on adsorption of the gas, *i.e.*, there would be a fall in temperature of the catalyst equal to the total rise observed in the series of adsorption experiments.

If, as is the case, the adsorption is not completely reversible, then the ratio of the fall in temperature on evacuation to the total rise in temperature observed during adsorption will be a rough measure of the extent to which the adsorption is reversible. To measure this fall in the temperature due to desorption the following procedure was adopted :—

After a series of admissions had been made, the catalyst was opened to the pumps, and the whole system was evacuated as rapidly as possible, the temperature recording system being left running. In all cases there was a rapid fall in temperature on applying the pumps, and this was measured and compared with the total rise which had taken place during the measurments of the heats of adsorption. Determinations of this kind were carried out for carbon monoxide on Catalyst B, and on the two pure oxides (Table VIII.), and for hydrogen on the mixed Catalyst B only (Table IX).

TABLE VIII.—CARBON MONOXIDE.

Expt. No.	Catalyst.	Total Vol. Adsorbed. c.c.	Total Rise in Temp. °C.	Fall in Temp. °C.	Fall / Rise.
H 6	Catalyst B	0·338	0·113	0·054	0·48
H 10	,, ,,	0·5168	0·203	0·065	0·32
K 6	,, ,,	0·6074	0·149	0·072	0·48
M 12	Zinc oxide.	0·317	0·318	0·131	0·41
M 14	,, ,,	0·227	0·263	0·097	0·37
N 7	Chromium oxide	15·96	0·966	0·034	0·04

TABLE IX.—HYDROGEN. (ZINC OXIDE—CHROMIUM OXIDE CATALYST B.)

Expt. No.	Total Vol. Adsorbed. c.c.	Total Rise in Temp. °C.	Fall in Temp. °C.	Fall / Rise.
G 8	0·367	0·131	0·016	0·12
H 3	0·330	0·092	0·016	0·15

Gases Given off on Activation.

Zinc Oxide—Chromium Oxide—Catalyst B.—After each series of admissions of carbon monoxide or hydrogen, the catalyst was reactivated by evacuating the whole system at room temperature and then heating the catalyst to 450° C. and pumping off the gases evolved as the temperature of the catalyst was raised.

If the temperature of the catalyst was raised slowly, at about 100° C., gas was evolved from the catalyst (varying from 0·07 to 0·15 c.c.) and then with a constant or very slowly rising temperature, the pressure in the system began to decrease, indicating the re-adsorption of the gas, until finally a hard vacuum was obtained. On raising the temperature still higher no

more gas was evolved until the temperature reached 400° C., when about 0·5 c.c. of gas was liberated.[11]

It was further observed that the gas evolved at the lower temperature range was not condensed by liquid air, whereas that evolved at the higher temperature was completely condensed by liquid air. All these phenomena were observed with both carbon monoxide and hydrogen. Data showing the way in which the gas was evolved and re-adsorbed are given for 175° C. (Table X).

TABLE X.—GAS PREVIOUSLY ADSORBED: HYDROGEN.

Temperature of Experiment = 175° C.

Time (min.).	Pressure (cm.).	Time (min.).	Pressure (cm.).
0	0·00036	30	0·00299
4	0·00654	35	0·00205
7	0·01545	40	0·00143
15	0·00936	50	0·00080
18	0·00777	60	0·00049
22	0·00575	75	0·000295
26·5	0·00397	91	0·000194

The rate of evolution of carbon monoxide or hydrogen is seen to be greater than the rate of adsorption. The existence of the phenomenon depends on this fact.

An attempt was also made to determine the nature of the gases evolved, both at the low and the high ranges of temperature. Since the gas evolved at low temperatures and later re-adsorbed was not condensed out by liquid air, and since, as was found by experiment, the evolution at 100° occurred only after adsorption of hydrogen or carbon monoxide, it is reasonably certain that the gas evolved consisted of unchanged hydrogen or carbon monoxide.

At 400°, the gas evolved was completely condensed out by liquid air. For further examination, it was drawn into a gas burette where it could be treated with lime, phosphorus pentoxide, or other absorbents. It proved to consist of either carbon dioxide or water. These observations indicate the occurrence of two modes of adsorption of hydrogen and carbon monoxide on oxide catalysts.

Zinc Oxide Catalyst.—The phenomenon of evolution and re-adsorption of gas was not observed in the case of the zinc oxide catalyst, and owing to its low adsorptive power, no attempt was made to determine the nature of the gases given off on activation.

Chromium Oxide Catalyst.—Owing to the strong adsorptive capacity of this catalyst for carbon monoxide, similar results to those obtained for the mixed oxide catalyst might have been anticipated.

Actually, when the chromium catalyst was heated up slowly, after 8-16 c.c. of carbon monoxide had been adsorbed, it was found that gas was slowly evolved even at 200° C. The volume evolved increased with increasing temperature, no re-adsorption of gas taking place.

The gas evolved was mainly, but not entirely condensed out by liquid air, indicating that the gas evolved was chiefly (80-90 per cent.) carbon dioxide, with some (10-20 per cent.) carbon monoxide.

[11] *Cf. Nature,* **126,** 352, 1930.

Summary.

The heats of adsorption and adsorptive capacity of hydrogen and carbon monoxide on the zinc oxide, chromium oxide, and zinc oxide-chromium oxide catalysts have been investigated, using the vacuum calorimeter previously described. The heats of adsorption range from 25 to 10 Cal./gm.mol., the maximum value being obtained for the first small quantities adsorbed.

The heat of adsorption of carbon monoxide on ZnO is the same as that on ZnO . Cr_2O_3, although the adsorptive capacity is much greater in the latter case. This indicates that the greater efficiency of the mixed catalyst is due to an enlargement of the internal area of the catalyst.

Chromium oxide and zinc oxide do not adsorb hydrogen so strongly as the mixed catalyst, but the former oxide adsorbs carbon monoxide very readily.

At low temperatures, hydrogen and carbon monoxide are mainly adsorbed without disruption of the molecules, but at temperatures of 100° and over, the adsorption is irreversible, and the gas can only be removed by heating to high temperatures as water and carbon dioxide respectively. In the case of the mixed catalyst, the rate of evolution of gas from one type of adsorbed film is greater than the rate of condensation to the second type of film, so that on heating in the neighbourhood of 100° C. of a catalyst which has adsorbed hydrogen at 20°, there occurs an evolution of hydrogen which is followed slowly by readsorption.

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THE RATE OF SORPTION OF AMMONIA ON MEERSCHAUM.

By Meredith Gwynne Evans.   ·

This work was undertaken in the hope that the time taken in the attainment of equilibrium would be sufficiently short to enable one to make rapid measurements of the heat of sorption by means of the Bunsen Ice Calorimeter. The system, however, took a considerable time to come to equilibrium, and complete measurements of the heats of sorption within the " life " of a Bunsen Ice Calorimeter were not possible. The system showed some remarkable characteristics, which were thought might be of interest in themselves.

Experimental.

The apparatus is shown in Fig. 1, and consists essentially of a gas measuring system and manometer and the sorption bulb.

The sorption bulb (S) was a small bulb of jena glass filled as completely as possible with powdered meerchaum. A small plug of glass wool was used to prevent the powdered meerchaum being carried over into the rest of the apparatus during the process of outgassing. The

tap T_1) enabled one to shut off the sorption bulb from the rest of the apparatus before the distribution of the gas. The gas burette and manometer were of the usual U-tube type, but because of the large amounts of gas that were dealt with, a large calibrated bulb (B) was employed as well as the burette. The gas burette was graduated in 1/10 c.c. and could be connected through the tap (T_2) to the gas train or to the pumping system as desired. The other limb of the manometer was evacuated, and the vacuum was preserved by means of a cocoanut charcoal bulb (C). A McLeod gauge in this portion of the manometer was used to keep a constant check on the vacuum.
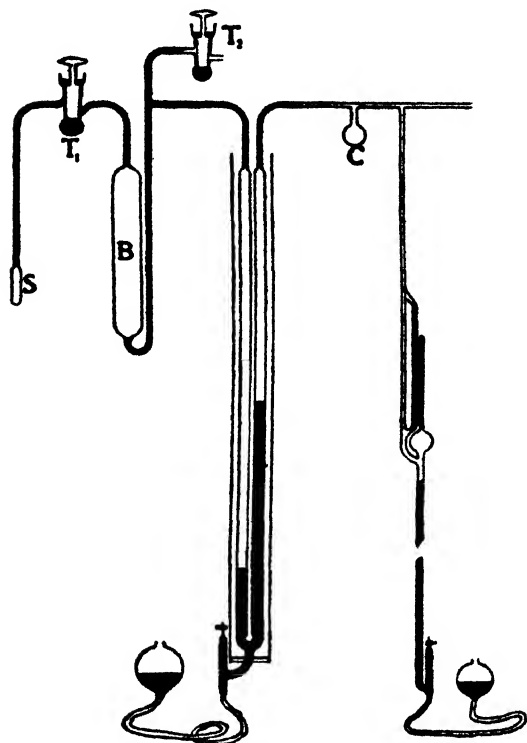
A glass scale accurately divided into millimetres was placed in front of, and as close as possible to the limbs of the manometer and burette. The whole of the gas and pressure measuring system was enclosed in a water bath kept at constant temperature by circulating water from a thermostat. The measuring system was illuminated by linolite lamps, which were water jacketed and observations were made by means of a reading telescope.

FIG. 1.

All capillary tubing used as connections was carefully calibrated in the usual way with mercury before being built into the apparatus. The gas burette was calibrated and the diameters of the burette and manometer limbs were determined at distances of 2 cm. along their lengths in order to make corrections for changes in capillary depression of the mercury due to changes in diameter of the tubes.

The Ammonia.—Ammonia was used since it has been found to give much greater sorption values than most other gases and also because of the ease of purification and manipulation. The ammonia was prepared by the method outlined by Burt and Francis [1] by making use of the decomposition of copper ammino-sulphates. It was stored in large bulbs which had been outgassed previously at 300° C. for several weeks. Every sample of gas was purified before admitting it to the apparatus, by condensing it at the temperature of liquid air on phosphorus pentoxide, which had been distilled in oxygen *in situ*. The presence of any permanent gas could be detected at this stage while the ammonia was

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[1] Burt and Francis, *Proc. Roy. Soc.*, 116A, 586, 1927.

solid by means of a McLeod gauge and could be pumped off by means of a mercury vapour pump.

The Meerschaum.—The meerschaum was the naturally occurring material and not artificial. The outer portion and any discoloured portions of the meerschaum were removed and the clean material was ground into a fine powder and used in this condition. The sorption of ammonia was followed after outgassing the meerschaum *in situ* at successively higher temperatures. The first temperature of outgassing was 250° C. and the meerschaum was pumped out at this temperature until, on heating in a closed system for twenty-four hours, no pressure could be detected on a McLeod Gauge. At 250° C. this process took a fortnight to complete, while at 300° C. outgassing was carried on for three weeks and at 450° C. only after six weeks could no pressure be detected. In the early stages of outgassing new meerschaum, water was freely given off and condensed in the cooler parts of the apparatus. Before any experiments were carried out after outgassing of the meerschaum, the apparatus, with Tap T_1 closed, was thoroughly exhausted, at the same time being heated to 100° C. to remove any moisture which might be adhering to the glass.

Experimental Procedure.—With tap (T_1) closed and with (S) and (B) surrounded by ice baths, gas was admitted to the measuring system through (T_2). When a desired initial pressure was developed, (T_2) was closed and the system left for three hours for the gas to come to the constant temperature of the baths. Readings were then made of the pressure and the volume of the gas, and when constant values were obtained (T_1) was opened, the time being noted, and the gas admitted to the sorption bulb. Readings of the volume and pressure of the gas were made at intervals, the time between the readings increasing as the process slowed down. The sorption bulb dead space was calibrated by means of helium. The helium was passed through a U-tube filled with charcoal which had previously been outgassed at 300° C. *in situ* and was now immersed in liquid air. It has been found that although this treatment removes most of the permanent gases other than helium it does not dry the gas, so after passing over the charcoal, the helium was passed over phosphorus pentoxide. Known volumes of helium at varying pressures were admitted to the sorption bulb and in each case time readings were taken for a considerable period, but no time effect was observed. The helium was admitted to the sorption bulb at different pressures, and at each pressure the same value of the dead space was given and there was no indication of any sorption of the helium.

Results.

As indicated the first sorption experiments were carried out after outgassing the meerschaum at 250° C. The results for the rate of sorption of ammonia with the meerschaum in this condition are shown in Fig. 2. In order to compress the time scale the logarithms of the sorption measured in cubic cm. of gas at 0° C. and 760 mm. pressure were plotted against the logarithm of the time measured in minutes. The curves obtained in the initial low pressure experiments rise rapidly at first, then bend over concave to the log time axis and eventually become almost parallel to the log time axis showing that equilibrium is being approached.

When it was evident from the curve that we were very near true equilibrium, tap (T_1) was closed and after a number of initial readings had been taken, more gas was admitted to the meerschaum at a higher pressure. It was found that at the high pressures the system did not approach equilibrium as rapidly as in the initial low pressure experiment. This can be seen in the two low pressure curves A and B in Fig. 2, where over comparatively linear portions of the curves — the slope of A between log t 1·3 and 2·5 is 0·0010 and for B between log t 1·8 and 3·0 is 0·0026. The next curves C and D obtained by successive addition of ammonia to the meerschaum at pressures of 460 mm. and 640 mm. respectively are of rather a peculiar type. Both these curves can be divided into two portions— the first portion is very similar in form to the lower pressure curves. At an early stage the curve seems to indicate a slow approach to equilibrium, but then a new portion appears where the slope of the curve increases, and then begins to bend over again concave to the log t axis, so that the second portion of the curve is in the form of a very flat S. These characteristics are very noticeable in curves C and D of Fig. 2. The first explanation of such behaviour which suggests itself is that this " irregularity " is due to a leak in the apparatus. But the apparatus was subjected to very stringent tests and was found to give no indications of a leak even after several weeks. The next series of curves (Fig. 3) show the results of sorption experiments carried out on meerschaum which had been out-gassed at 300° C. for a month.

Here we see the same features as we have discussed for the previous set of curves. The effect of increasing the temperature of outgassing, however, has been to lower the sorptive capacity of the meerschaum. The change in the rate of approach to equilibrium with increase in pressure, is clearly seen in the first two low pressure curves of this series, and the two high pressure curves show the same peculiar inflection as those in Fig. 2, the effect being again more marked in the final high pressure curve.

The meerschaum was next outgassed at 450° C., a process which took six weeks, to complete. It was found that this further heat treat-

FIG. 2. (See Table II.)

ment had considerably lowered the sorption capacity of the meerschaum. The initial experiment with the meerschaum in this condition was carried out at a final pressure of 137 mm. but in spite of this higher pressure, the sorption is considerably lower than in the previous cases.

Comparing the initial sorption experiments at pressures of 19 mm., 13 mm. and 137 mm. after outgassing at 250° C., 300° C. and 450° C. respectively, we find that these curves show the progressive decrease in sorption with increase in the temperature of outgassing. Moreover, the shape of the initial low pressure sorption curve has changed and this low pressure curve now shows the charac-teristics which were

FIG. 3.   (See Table III.)

associated with the higher pressure curves in the previous series (Fig. 4).

In this series of experiments it was decided to remove the ammonia at a slightly lower temperature than the outgassing temperature *viz.*, 450° C., and carry out each experiment *ab initio*. It was found possible to remove all the ammonia sorbed at 400° C. without altering the con-dition of the sorbent. Fig. 4 shows the results obtained and we find the same type of inflec-tion in all these curves.
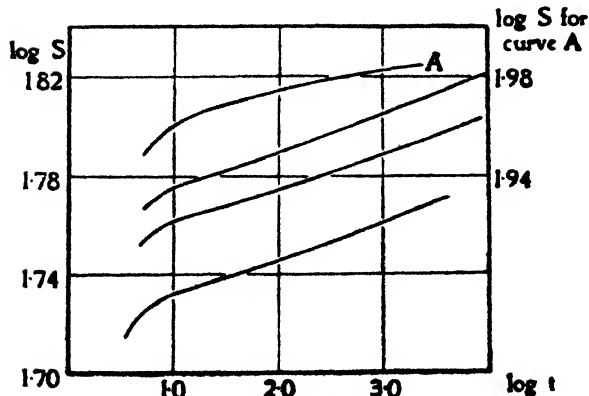
FIG. 4.—Curve A of Fig. 2 is shown for comparison.

The Freundlich Isotherm.

Since the apparatus was not a constant pres-sure apparatus, it is ne-cessary to assume that the sorption which occurs at a definite final pres-sure is that which would have occurred had that final pressure been the constant pressure throughout the whole of the experiment.   Making this assumption it is possible to obtain a series of total sorption-pressure data.   Where sorption at higher pressures has been carried out by successive addition, the assumption is made that any particular sorption is the sum of the sorption at that pressure and those at lower pressures of the same series.

TABLE I.—*S* IN C.C. AT 0° C. AND 760° C.

Series 1. Outgassed at 250° C.			Series 2. Outgassed at 300° C.			Series 3. Outgassed at 450° C.		
S.	Total *S.*	Final Press.	*S.*	Total *S.*	Final Press.	*S.*	Total *S.*	Final Press.
		mm.			mm.			mm.
96·49	96·49	19·3	66·84	66·84	13·1	59·05	59·05	187·9
51·23	147·72	216·5	54·98	121·82	222·2	63·61	63·61	204·2
21·60	169·32	459·3	19·23	141·05	484·0	66·22	66·22	250·7
7·82	177·14	639·5	8·26	149·31	716·8			

The curves are shown in Fig. 5 plotting log *S* against log *p*.
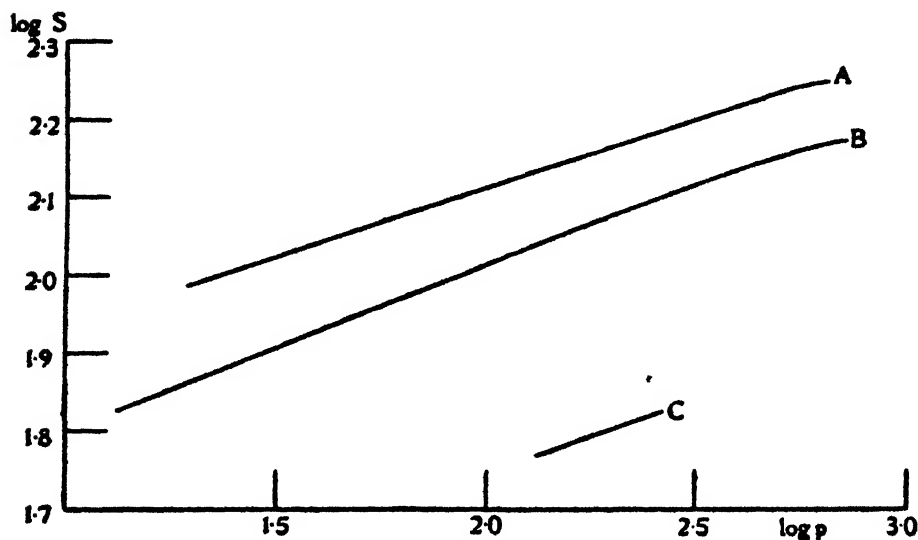
FIG. 5.

The curves A and B are good approximations to straight lines over a fairly large pressure range bending over slightly, at higher pressures : concave to the log *p* axis.

Increasing the temperature of outgassing (as seen by comparing A, B and C) does not affect the slope of these curves greatly, only shifting their positions with respect to the log *S* axis by lowering of the sorption.

The slope of these curves, or if we employ the Freundlich equation $S = kp^{\frac{1}{n}}$. the values of $\frac{1}{n}$ are :—

for A = 0·179 ; for B = 0·209 ; C = 0·194.[2]

[2] Compare Chappuis, *Wied. Ann.*, 19, 21, 1883 $\left(\frac{1}{n} = 0·184\right)$
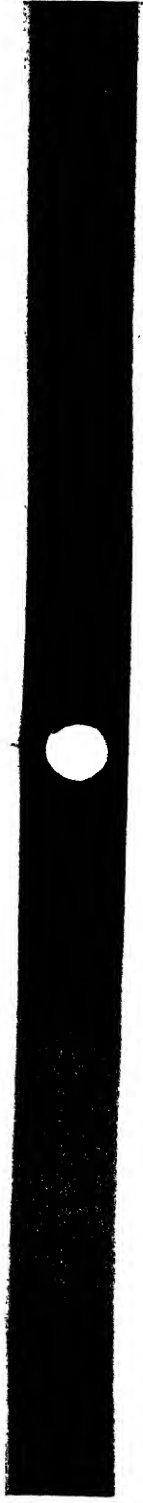
No. 1.

Before Sorption.

No. 2.

After Sorption

Fig. 6.

Theoretical Conclusions.

The peculiar shape of the log s/log t curves obtained at high pressures after outgassing at 250° C. and 300° C. and at all pressures after outgassing the meerschaum at 450° C. seems to indicate a change in the sorption process after a certain amount of gas has been taken up by the sorbent. One process seems to approach completion before the second process starts. Such a state of affairs, if it does exist, can only be due to the sorbent. Meerschaum has been shown by many workers to exist in a crystalline form known as sepiolite as well as in the amorphous form. Common forms of meerschaum are not wholly crystalline, but consist of a crystalline portion, found from its optical properties to be identical with sepiolite, and an isotropic constituent of the gel nature.[3] Fig. 6 shows X-ray powder photographs of the meerschaum we employed before and after sorption. In both photographs we find a few rather faint lines indicating the existence of the crystalline constituent. The absence of numerous sharp lines indicates the amorphous character of the bulk of the material.

So here we may assume we are dealing with a heterogeneous sorbent and we can see how the peculiar curves of the log S/log t relationship might arise.

Let us assume that the gel constituent has a greater activity and greater sorptive power than the crystalline portion ; then at first sorption will occur on the gel to such an extent that sorption on the crystalline portion is entirely masked or non-existent—the state of affairs represented by the initial low pressure curves. As we add ammonia by successive additions, we approach a state in which the gel is nearly saturated with gas, and then sorption on the crystalline portion becomes under increased pressure a perceptible process. This state will be represented by the higher pressure curves.

When we consider the progressive desiccation of the sorbent it is reasonable to suppose that the removal of water does not affect the sorptive capacities of the gel and the crystalline constituents in the same way. There is abundant evidence that the removal of water from gels and amorphous materials lowers their sorptive capacities. But on removal of the water from sepiolite, this crystalline material is capable of taking up various vapours and gases.

In fact sepiolite seems to behave in very much the same way as the zeolites and the removal of water increases the sorptive capacity.

So as we remove water from meerschaum by increasing the temperature of outgassing, the sorptive capacity of the gel constituent will probably decrease, while that of the crystalline constituent will increase. This would account for the occurrence of the point of inflection in the log S/log t curves at a much lower pressure after outgassing at 450° C. since the sorptive capacities of the gel and crystalline constituents are converging.

Summary.

(1) The rates of sorption of Ammonia on Meerschaum have been studied and the nature of the log S/log t curves has been found to be dependent on the temperature at which the meerschaum is outgassed.

[3] Michel, *Z. Kolloid*, **12**, 165, 1912-1913.

(2) The log S/log p relationship has been found to be linear over a fairly large pressure range, deviation from linearity occurring at higher pressures. The dryness of the sorbent affects the total quantity of ammonia sorbed. The sorption decreasing with increased dryness.

(3) A tentative theory to explain the peculiar rate curves is based upon the crystalline and gel constitution of meerschaum. X-ray powder photographs of the sorbent have been taken to confirm the idea of the heterogeneous nature of the Meerschaum.

Appendix.

The experimental values relating to Figs. 2 and 3 are given hereunder by way of example :—

TABLE II.—MEERSCHAUM OUTGASSED AT 250° C. (FIG. 2).

Final Pressure. 19·3 (Curve A).		Final Pressure. 216·5 (Curve B).		Final Pressure. 459·3 (Curve C).		Final Pressure. 639·5 (Curve D).	
log S.	log p.	log S.	log t.	log S.	log t.	log S.	log t.
1·8515	0·000	1·5683	0·301	1·1879	0·000	0·7745	0·301
1·9490	0·699	1·5905	0·477	1·2462	0·602	0·8209	0·477
1·9601	1·000	1·6314	0·903	1·2608	1·000	0·8470	0·699
1·9650	1·176	1·6489	1·176	1·2632	1·301	0·8549	1·000
1·9676	1·398	1·6591	1·431	1·2695	1·477	0·8573	1·176
1·9719	1·778	1·6669	1·653	1·2725	1·699	0·8591	1·477
1·9746	2·021	1·6770	2·000	1·2777	1·954	0·8597	1·778
1·9775	2·330	1·6870	2·332	1·2869	2·322	0·8691	1·954
1·9795	2·598	1·6998	2·854	1·2943	2·519	0·8887	3·013
1·9845	3·337	1·7096	3·321	1·3345	3·433	0·8932	3·172

TABLE III.—MEERSCHAUM OUTGASSED AT 360° C. (FIG. 3).

Final Pressure. 13·1.		Final Pressure. 222·2.		Final Pressure. 484·0.		Final Pressure. 716·8.	
log S.	log t.	log S.	log t.	log S.	log t.	log S.	log t.
1·7312	0·301	1·4995	0·000	1·7761	0·301	0·7839	0·301
1·7672	0·602	1·5901	0·477	1·1942	0·477	0·8248	0·471
1·7804	1·000	1·6271	0·778	1·2079	0·699	0·8325	0·699
1·7888	1·301	1·6136	1·000	1·2172	1·301	0·8357	1·176
1·7960	1·602	1·6571	1·398	1·2227	1·778	0·8414	1·477
1·8065	2·079	1·6810	1·602	1·2380	2·431	0·8519	2·079
1·8107	2·322	1·6970	1·954	1·2531	3·090	0·8597	2·380
1·8137	2·477	1·7126	2·332	1·2632	3·167	0·8825	3·033
1·8228	3·033	1·7284	2·799	1·2767	3·455	0·9063	3·391
1·8251	3·225	1·7402	3·290	1·2840	3·633	0·9170	3·598

SPIERS MEMORIAL LECTURE:
MICHAEL FARADAY.

By ROBERT LUDWIG MOND, LL.D., M.A., F.R.S.E.,
President of the Faraday Society.

The second Spiers Memorial Lecture (delivered in accordance with the terms of a Trust founded to keep alive the memory of the late Frederick Solomon Spiers, a founder of the Faraday Society in 1903 and its secretary and editor throughout the period of its history until his death on 21st May, 1926) was given in the lecture theatre of the Royal Institution, Albemarle Street, London (by kind permission of the managers) on Wednesday, 17th June, 1931, at 5·50 p.m. by Dr. R. L. Mond (President of the Faraday Society), who took as his title " Michael Faraday." Professor F. G. Donnan, a past President of the Faraday Society, occupied the Chair.

Dr. Mond, before proceeding to give his lecture, expressed his appreciation, as President of the Faraday Society, of the privilege of holding this meeting in the lecture theatre of the Royal Institution. The privilege was the greater since the Faraday Society was the first body, other than the Royal Institution, to hold a meeting in the theatre since its reconstruction.

Dr. Mond also wished to express, on behalf of all present, hearty congratulations to the distinguished Director of the Royal Institution and of the Davy-Faraday Laboratory, Sir William Bragg, on whom had been conferred the Order of Merit.

At the conclusion of the lecture Professor Donnan, in proposing a vote of thanks to the lecturer, said that all would agree that it was a very fortunate idea on the part of Dr. Mond to devote his lecture to the memory of Faraday as a man, especially in view of the happy setting which had been given to the lecture in Faraday's own lecture theatre. The lecture was full of evidence of the modest character of Faraday. This subjectcould have been treated by no one more fitted than their modest lecturer.

The Faraday Society was very pleased and highly honoured that Dr. Mond should be their President during the year 1931. It would be known to all that the lecturer had devoted his life to scientific objects. He was the worthy son of a distinguished father—it must be remembered that it by no means necessarily followed that a son would be worthy to follow in the footsteps of his father. Dr. Mond's fine work for science was particularly recognised within the Royal Institution. Then, again, he was very interested in archæological science ; not merely had he financed expeditions, but he himself had taken an active part in them. His interests did not cease there ; he was a great amateur of the arts as well as of all the sciences ; he had concerned himself keenly in the hospitals and like interests in this country and in France. Professor Donnan added that he had had frequent opportunities of conversing with the lecturer, and it seemed impossible to come to the end of his learning, and yet Dr. Mond was always engaged in some activity, and it was very difficult to see how he found time to come by so much learning.

Sir William Bragg, in seconding the vote of thanks, welcomed the opportunity of saying something about the lecturer.

During 1931 those present would be hearing a great deal about Faraday, but he believed that they would not get tired of him, because every one who attempted to give an impression of Faraday's rich life showed a new picture. He had been particularly interested in the picture which Dr. Mond had portrayed.

The Royal Institution owed so much to Dr. Mond that he was particularly glad to be able to express their thanks on this account also. The whole of the work of the Davy-Faraday Laboratory was due to Dr. Mond and his father. Dr. Mond, moreover, when it became necessary to rebuild the theatre in which they were then sitting, had with his usual modesty and generosity, come to their assistance.

He felt it very difficult to say why it was that the Royal Institution had had such an immense influence upon the scientific work of the country—if any doubted that influence he would invite them to walk through the gallery which surrounded the theatre, where they would see a historical survey, illustrated by the original apparatus, of the work that had been done in the building. Without any doubt much of the best scientific work of the last century in England had come from the laboratories of the Institution. It was very strange that the Institution had developed into such a tremendous force—along lines quite different from those contemplated at the time of its foundation. Whatever the explanation might be, they would always be proud that the Institution gave Faraday his chance, and that Faraday took it.

The motion was received with acclamation, and Dr. Mond, in reply, said that he had felt it a great responsibility to stand at Faraday's table and speak of him. Sir William Bragg, following in Faraday's footsteps, had become used to the position, but to any other speaker it required some courage—and he had it. Faraday was a man of phenomenal courage and great ideas. In addition to the responsibility, he (Dr. Mond) had felt it an immense privilege to lecture. In his time he had helped others with their experiments, and in particular he remembered some of the lectures of Dewar and of Nicholas Tesla. He recalled how Lord Kelvin was sitting in the Chair when Dewar showed liquid air for the first time, and how charmingly Lord Kelvin had played up to the lecturer, to the consternation of Lady Kelvin, when he was invited to drink from a champagne glass some liquid air. He recalled, too, the precautions they took when fitting up Tesla's apparatus for his experiments, when they all stood in danger of immediate electrocution if anybody had been careless. This theatre, however, was full of memories.

Professor Donnan had made flattering allusions to the extent of his knowledge ; for himself he only realised how much there was that he did not know, and he was still looking forward to learning more.

Professor T. M. Lowry, a past President of the Society, proposed the thanks of the Society to the director and managers of the Royal Institution for their great kindness in allowing the lecture to be held in their theatre. The first Spiers' Memorial Lecture had been given three years ago at the same table. He thought it was proved that the Faraday Society had been very fortunate in its choice of a name.

The motion was briefly seconded by Mr. Emile Mond.

MICHAEL FARADAY.

We have had the temerity to name our Society after Faraday.   As those Sciences which are our particular field of study owe so much of their inception and development to his master mind, this name gives a far better description of their scope than any more technical and limited definition.

But in accepting the name of Faraday, we have not only defined our activities, but also, we have undertaken, as far as lies in our power to bring to our problems, that openmindedness, that innate sense of justice and impassioned love of truth for its own sake, which makes his figure stand out beyond that of his compeers.   I believe that I do not presume, when I undertake on your behalf, to dedicate ourselves again to this task.

When I think of Spiers, in whose memory we are united to-day, and to whose unceasing activity the successful development of our Society is so largely due, I feel that he is with us here in spirit ; and that this opportunity of our restating the debt we feel we owe to Faraday, would have been uppermost in his mind.

We are preparing to celebrate the centenary of one of the most fruitful conceptions of the human mind.   Many of those most qualified to speak will, within the coming months, comment on the origin of this conception and its subsequent development and its so manifold applications, that it is difficult for us to imagine ourselves deprived of the untold benefits we owe to it.

But there is one aspect of this triumph of the human mind, which deserves our special consideration, namely the study of the conditions and of their influence on the individuality which made the conception a possibility.

Faraday's ancestors, who hailed from Yorkshire, belonged to that class of artisans, whose innate honesty, sturdy independence, and stead- fast industry did much to convert England from a purely agricultural to a leading industrial country.   This feeling of independence, which had helped in the Reformation and developed the Nonconformist movement, led to the formation of smaller religious subdivisions, to one of which, the Glassites or Sandemanians, Faraday's family belonged, and of which he became the most distinguished elder.

The Sandemanian form of belief, which combines (like that of the Quakers and Unitarians) a great simplicity of mind with exemplary conduct and love and esteem for your fellow members, must have had a dominating influence in the atmosphere of his upbringing.   His great and undivided devotion for his mother (as witnessed by his letters), his love for his wife, and his affection for his sisters, all contributed to that serenity and purity of thought which pervaded his life.

His early education, his apprenticeship as a bookbinder, his early contacts with elementary science, especially his active membership of a youthful philosophical debating society, moulded his mind to that unselfish devotion to the search of truth for its own sake, which was to be so richly rewarded in his future career.

Spinoza, in his essay on the human understanding, suggests, as a working rule for human conduct, the imagining of a character strong in those points where one is aware of one's weaknesses, and the desire to emulate that character. This is what Faraday did, when first he realised the weak points of his education; his prolific correspondence bears witness to his heroic efforts to obtain command of the power of self-expression, both in writing and speech. Faraday himself refers to this in a letter:

"My store of learning respecting knowledge, abstractedly considered, has been gathered, some time since, from the writings of Lord Bacon, and from a work by Dr. Watts, 'On the Improvement of the Mind,' which I consider so good in its kind that no person ought to be without it."

"And here I must be allowed to say, that it is my firm belief, that were all the benefits which may be derived from a vigorous exercise and enjoyment of the powers and privileges of the City Philosophical Society well known and duly appreciated, each member would feel eager to share in the general good they present, and regret that such estimable advantages had been until now suffered to remain unemployed. For myself, I have perceived and used them; and it is but natural that one who has gained much by the Society should feel grateful for it, and endeavour to express it in terms of praise and respect. It has increased my store of mental enjoyment, and as it has taught me liberality I recommend it liberally to others. Nor can I refrain from saying that I know no institution, with means so small and professions so humble, calculated to produce so much effect or results so highly valuable.

"I trust I shall be excused for the warmth of my feelings on this occasion. I do not express myself thus because I imagine you are not conscious of the true value of the Society; but having experienced to a great extent its beneficial effects, I am willing to testify my consciousness of them. I shall now consider the means of obtaining knowledge:

By Conversation.

"It is with regret I observe that so little are our private evenings for conversation appreciated, that not one half of our members generally attend.

". . . For my own part, so highly do I value the opportunities of our conversations, that I would rather be absent on any lecture night than on a private evening.

By Lecturing.

"As practised at this Society, lecturing is capable of improving not only those who are lectured, but also the lecturer. He makes it, or he ought to make it, an opportunity for the exertion of his mental powers, that so by using he may strengthen them; and if

he is truly in earnest, he will do as much good to himself as to his audience. . . .

By Reading.

" With our parsimonious and economical subscriptions it can scarcely be imagined that to apparatus, lectures, and conversations, a library should be added. . . .

By Observation.

" There is one peculiar branch of it for which we possess facilities as a body which many of us do not as individuals ; I allude to the making of experiment. . . .

By Study.

" Our Society is not at all deficient in those means which encourage a disposition to study : I refer more particularly to the portfolio, which has been established for the reception of such papers, analyses, or essays, either on lectures, questions, or independent subjects as may be contributed by the members. This portfolio supplies the place of a report, and each one who comes forward is asked to place in it either his question or lecture ; or, if he please, any original paper, so that it should really be the archives of the Society. It circulates among the members with the books of the library. . . . I will not detain you longer, gentlemen, from the expressions of your opinions on this subject, than to point out to you two modes in which you may treat it. The question may be formally put, whether the means of acquiring knowledge which I have pointed out are sufficient to the extent that I have described ? Or, as I should rather wish it, the conversation may turn on the means afforded by the organization of the Society ; and on such improvements of those means as may suggest themselves to the members as being practicable. . . . "

What his fellow-members think of him is best expressed by the following poem by Dryden, written in 1817 :

" But hark ! A voice arises near the chair !
Its liquid sounds glide smoothly through the air ;
The listening Muse with rapture bends to view
The place of speaking, and the speaker too.
Neat was the youth in dress, in person plain ;
His eye read thus, Philosopher in grain ;
Of understanding clear, reflection deep ;
Expert to apprehend, and strong to keep.
His watchful mind no subject can elude,
Nor spacious arts of sophists e'er delude ;
His powers, unshackled, range from pole to pole ;
His mind from error free, from guilt his soul.
Warmth in his heart, good humour in his face,
A friend to mirth, but foe to vile grimace ;
A temper candid, manners unassuming,
Always correct, yet always unpresuming.
Such was the youth, the chief of all the band ;
His name well known, Sir Humphry's right hand.

With manly ease towards the chair he bends,
With Watt's logic at his finger-ends.
' I rise (but shall not on the theme enlarge)
To show my approbation of this charge :
If proved it be, the censure should be passed,
Or this offence be neither worst nor last.
A precedent will stand from year to year,
And 'tis the usual practice we shall hear.
Extreme severity 'tis right to shun,
For who could stand were justice only done ?
And yet experience does most clearly show
Extreme indulgence oft engenders woe.
In striving then to hit the golden mean—
To knowledge, prudence, wisdom, virtue seen—
Let Isaac then be censured, not in spite,
But merely to evince our love of right.
Truth, order, justice cannot be preserved,
Unless the laws which rule us are observed.
1 for the principle alone contend,
Would lash the crime, but make the man my friend.' "

It was of immeasurable value that a man of Faraday's proclivities should, early in life, have become associated with one of the greatest genius of his time, Humphry Davy. Davy, with a slightly differing upbringing, and coming into contact with Chemistry through elementary Pharmaceutics, knew how to utilise his opportunities in a Pneumatic Institute, to unfold the secrets of the Oxides of Nitrogen, and rising from power to power, revealing the composition of the Salt, Chlorine and its compounds, discovering Potassium and Sodium, the Alkaline Metals, and incidentally, the Electric Arc ; raising the Royal Institution, from a bankrupt Mechanics Institute, into one of the most powerful centres for the exposition of light and learning. Here it was that Faraday found him, in time to hear his last lectures, and here he sent to him his application for a position, accompanied by his bound copy of the notes of those lectures, which led to Davy taking the first opportunity of gratifying his wish, and it was from here that Davy took Faraday on his celebrated journey, which brought him into touch with different countries, people and the leading men of science : an enlargement of his vision, which was to his unbounded benefit to him, as witnessed by what he did, and did not, write in his letters.

The opportunity he had to assist Davy in working on the properties of Iodine, in contact with the best French chemists, afforded him the opportunity of studying the mental reactions of the best minds.

Faraday's return to the Royal Institution gave him the opportunity to assist in the development of the Safety Lamp. As a working example in its successive phases, of the application of a simple principle, namely that combustion requires a minimum temperature for its maintenance, and of its converse, there are few more beautiful instances ; the case in the passage outside illustrating the experimental evolution of the cooling effect of apertures, from a single copper tube to a wire gauze, is an object-lesson of unique value.

Faraday's habit of noting and describing with great accuracy every idea, action or experiment aided him both to correct his shortcomings

and observe his progress. (He often refers back in future years to his past mistakes, as especially useful for his development.) This led to his being entrusted by Brande with the editorship of the *Quarterly Journal of Sciences*, a task which kept him in touch with current thought and work.

From Faraday's first paper in 1816 on Caustic Lime, to his last in 1857, on the experimental relations of Gold and other Metals to light, we follow step by step, not only the growth of his self-assurance in his power of compelling nature to respond to his questions, but also his unceasing endeavours to satisfy his conviction that all the Natural Phenomena (Chemical Affinity, Light, Heat and Pressure, and Electricity and Magnetism in their various manifestations) were different aspects of the same Force.

This mental attitude was already defined in his lecture to the City Philosophical Institute, at the age of twenty-seven, and amplified in his course of lectures on the various Forces of Matters (in 1859-60), thirty-one years later. Extraneous researches (such as his work on Silversteel, and similar alloys, different glasses (including heavy glass) ; the discovery of Benzol and the liquefaction of gases (under the impulse of Davy) were minor adjuncts to the logical evolution which, through the study of Statical Electricity, the comparison with that produced by the Voltaic Cell, led to the discovery of the fundamental laws of Electro-Chemistry, and subsequently to the study of the relationship of Electrical and Magnetic Phenomena, leading to the recognition of Para- and Dia-Magnetism and of Specific Inductive Capacity, and thence, through the Phenomena of Induction, to the Production of the Electro-Magnet, and Electromagnetic Rotation, leading to the culmination of the action of his induced electromagnetism on the rotation of Polarized Light, thus triumphantly proving the Unity of Force in its many manifestations.

This search for the fundamental relations led him to assume fundamental conceptions as to the manner in which such forces manifested themselves, and the study of the *magnetic* fields of force, as illustrated by the iron filings, suggested to him *electric* fields of force which, when clad in mathematical formula, by the expert hands of Clark Maxwell, laid the foundation of our modern conceptions of the action of forces at a distance.

Although Faraday, through his association as assistant and lecturer (both at the Royal Institution and at Woolwich), and as editor of the Royal Institution Publications, and by his voluminous reading, as well as by his active correspondence and contact with other workers in the scientific fields, kept in continuous touch with current progress, his own work is singularly little influenced by or based upon the results of his fellow-workers. It is only when questions of priority arise that it becomes evident that he is keeping in touch with current thought. His characteristic procedure continually to check any theory by, what were for him, crucial experiments, led him to accept unhesitatingly the results of these experiments, whether in consonance with his preconceived opinions or not. The inherent honesty of his mentality, his great power and precision as an experimenter enabled him continually to check his hypotheses and avoid the pitfalls of preconceived notions.

I believe I am not overstating the case, when I express my belief, that many, if not most, of his enormous achievements are due to this fact.

The modesty of his life and of his requirements of it, and the happy and serene conditions under which it was spent, even when his closing days were darkened by his increasing loss of memory, prevented the intrusion of those disturbing factors which diminished the fruitfulness of the closing years of Humphry Davy's life.

In these few words on Faraday's career, I have assumed a knowledge of his Life and Work, which those of you who do not already possess it, will have ample opportunity to acquire within the next few months.

I shall hence proceed to examine the main proposition I propose to consider to-day, namely " What can we learn from Faraday's career, that we can usefully apply both to the search for new knowledge, the Perfection of that which we all possess, and the Perfectability of those who are devoting their lives to this research."

Faraday, in spite of being one of the greatest lecturers, both for young and old of all times, never produced a disciple to follow in his footsteps; although none of us can say how we are, consciously, sub-consciously or unconsciously inspired by his example. As the originator of lectures for children, he was very strongly convinced of the immense value of lectures, adequately illustrated by experiments, for arousing the spirit of inquiry in children.

Neither Faraday nor Davy commenced serious scientific study early in life. (Davy was born in 1779, and became assistant lecturer of the Royal Institution in 1801 at the age of twenty-two, having discovered nitrous oxide at the age of twenty.) Faraday was born in September, 1791. He was engaged by Sir Humphry Davy in March, 1813, as lecturer assistant, and his first paper was published in 1818, i.e., at the age of twenty-seven.

A view which dominates the modern pedagogic attitude towards Science is based on the early acquisition of a scientific training, with adequate laboratory facilities, as provided in our Public, Grammar and County Council Central Schools, and Institutions of similar character ; the knowledge thus acquired and ascertained by systems of Examinations being the stepping stones to more advanced training.

Would such a training provide us with a Faraday ? Professor Ostwald, in his admirable study of the life of Faraday remarks :

> " The question how Faraday would have reacted as a pupil of a Central School does not arise, as he never visited one, and he belongs to that type whose life is made very difficult in modern Germany, to its grave disadvantage as a nation, namely of men with an irregular education. My personal experience has induced me to act especially amicably towards such persons, whenever I have the opportunity, and the ' Mania ' of our ' High Schools ' to lock the door upon all those desiring to learn, who have not followed the orthodox and most inappropriate course up to the *Abiturienten Examination* robs the German nation of a group of recruits whose ranks would surely furnish more Generals than are produced by those of the normal students."

My father always strongly held the view that the successful prosecution of Scientific Work required the acquisition of power and the application of broad philosophical principles, of which the actual Scientific Facts were only the illustration, and that with the exception of a few precocious minds (to which class incidentally, he belonged, having gone

to the University of Marburg at the age of fifteen and having been at Heidelberg from sixteen to eighteen), the normal mind of the young was not sufficiently developed either to be able to grasp or to make use of the underlying philosophical generalizations and conceptions.

In this conception I fully concur. Anyone who has had an opportunity of observing the career of the young testers in chemical works will quickly realise the facility of teaching them even a fairly complicated technique; but how rarely, in spite of all endeavours, this early attainment leads to any subsequent progress. From Faraday's evidence before the Public School Commission in 1862, we may obtain an inkling of how he would have liked to be taught and the method of that teaching :

> " The object of education should be to train the mind to ascertain the sequence of a particular conclusion from certain premises, to detect a fallacy, to correct undue generalizations, to prevent the growth of mistakes in reasoning. Everything in these things must depend on the spirit and the manner in which the instruction itself is conveyed and honoured. If you teach scientific knowledge without honouring scientific knowledge as it is applied . . . you do more harm than good. You only discredit both the study and the parties concerned in it. . . . I never yet found a boy who was not able to understand by simple explanation and to enjoy the point of an experiment. I do think that the study of natural science is so glorious a school for the mind that, with the laws impressed on all these things by the Creator, and the wonderful unity and stability of matter, and the forces of matter, there cannot be a better school for the education of the mind. Persons who have had the discipline of classical instruction . . . persons who have been fully educated by the present system . . . are ignorant of their ignorance at the end of all that education. That happens with men who are excellent mathematicians. Until they know what are the laws of nature, and until they are taught by education to see what are the natural facts, they cannot clear their minds of absurd inconsistencies. . . . "

> " . . . The term ' training of the mind ' has for me a very indefinite meaning. . . . What does mind learn by that training? To be attentive, to be persevering, to be logical. But does it give that training of the mind which enables a man to (assign) a reason in natural things for an effect which happens from certain causes? It is the highly-educated men that we find coming to us again and again asking the most simple question in chemistry or mechanics. . . . I find their minds deficient (though) in their own studies.

> " Who are the men whose powers are really developed? Who are they who made the electric telegraph, the steam engine and the railroad? Are they the men who have been taught Latin and Greek? Are they Stephensons? . . . I have never had an opportunity of learning that kind of knowledge from the schools. . . . "

Now Faraday was possibly the individual who, by his efforts, has most widened the foundations of human knowledge. How did this young bookbinder assistant succeed in doing so? He, himself, discusses this problem. . . . First, he describes himself in a letter to De La Rive in 1858. He mentions that it was

> " in those books, in the hours after work that I found the beginning of my philosophy. There were two that especially helped me, the

Encyclopædia Britannica, from which I gained my first notions of electricity, and Mrs. Marcet's *Conversations on Chemistry*, which gave me my foundation in that science.

" Do not suppose that I was a very deep thinker, or was marked as a precocious person. I was a very lively imaginative person, and could believe in the *Arabian Nights* as easily as in the *Encyclopædia*. But Facts were important to me, and saved me. I could trust a fact, and always cross-examined an assertion. So when I questioned Mrs. Marcet's book by such little experiments as I could find means to perform, and found it true to the facts as I could understand them, I felt that I had got hold of an anchor in chemical knowledge, and clung fast to it. Thence my deep veneration for Mrs. Marcet—first as one who had conferred great personal good and pleasure on me ; and then as one able of knowledge which concerns natural things, to the young, untaught and inquiring mind.

" You may imagine my delight when I came to know Mrs. Marcet personally ; how often I cast my thoughts backward delighting to connect the past and the present ; how often, when sending a paper to her as a thank-offering, I thought of my first instructress, and such like thoughts will remain with me.

" I have some such thoughts even as regards your own father ; who was, I may say, the first who personally at Geneva and afterwards by correspondence, encouraged and by that, sustained me. . . ."

And what does the ripened mind of Faraday demand of education :

" The education which I advocate," says Faraday, " will require patience and labour of thought in every exercise tending to improve the judgment. It matters not on what subject a person's mind is occupied, he should engage in it with the conviction that it will require mental labour. Because the education is internal, it is not the less needful ; nor is it more the duty of a man that he should cause his child to be taught, than that he should teach himself. Indolence may tempt him to neglect the self-examination and experience which form his school, and weariness may induce the evasion of the necessary practices ; but surely a thought of the prize should suffice to stimulate him to the requisite exertion ; and to those who reflect upon the many hours and days devoted by a lover of sweet sounds to gain a moderate facility upon a mere mechanical instrument, it ought to bring a correcting blush of shame if they feel convicted of neglecting the beautiful living instrument wherein play all the powers of the mind. . . ."

Now, here we have two clues ; one the desire to test the knowledge ; and secondly, reverence for the teacher.

Of the first, Ostwald points out :

" The journey with Davy was for Faraday a high school of incomparable value. Through him, he came in contact with nearly all those who had accomplished scientific achievements and, owing to Davy's predilection, to carry on Research everywhere with a travelling experimental outfit, Faraday was able to acquire a freedom and ability in the shaping of crucial experiments, which would have taken many years to develop in a better equipped stationary Labora-

tory. It is the variety of Problems and the necessity to explore them mentally so that the query could receive a reply, with the limited means at his disposal, which are the characteristics of the scientific technique to which Faraday owes his subsequent great successes."

Reverence either to his Creator, for the beauties of Nature and the Laws which controlled them, for those from whom he learned and even for the little ones whom he taught, runs like a *leit Motiv* through his works and letters.

It has been my great good fortune to have been allowed a share of that friendship which many great thinkers had for my father, and the one common thread which ran through their lives was reverence for those who had taught them and for those in whose footsteps they walked and of the truths they were slowly unfolding.

It is this reverence which is Faraday's greatest legacy. It arouses in us a desire to appreciate and understand the working of their minds; and by obtaining an idea of how those minds gain the ascendency over their problems, are we emboldened to attempt to solve those that confront us.

In this connection, I welcome the holding of a Congress of Scientific History at the end of this month, and I hope that many of my fellow-members will find the time to be present.

Now, what steps if any can we take to smooth the path and guide the footsteps of those, of whom we hope that they will emulate our great prototype?

In early youth, we have to stimulate their interest by easy and well-illustrated lectures. We have to encourage the child's desire to experiment for itself. We have to guide this general education, not to teach science, but to develop the reasoning faculty and also the knowledge of languages (especially their own); so that when the time has arrived when the adult mind can commence to deal with broad philosophical ideas, the groundwork will have been prepared for it. The conception that science can be acquired by systematic education in either allopathic or homeopathic doses measured by the yardstick of examination must be definitely abandoned.

The outlook of scientific progress, brilliant as it may seem, is on the verge of a great crisis. The constantly-increasing ramifications leading to greater and greater specialization; the continually increasing demand of space, time, and money for the adequate experimental equipment, render it increasingly difficult to ascertain and obtain the experimental results which are required for the progress of scientific thought. The inception of scientific thought, as I hope I have succeeded in proving to you, depends so largely on the feeling of reverence both for the subject and its searchers.

This feeling can only be properly stimulated by giving the promising student the opportunity of studying at close quarters the operations of the great minds. Hence, I can now define our task: " How to bring the great pupil to the great teacher." It will be by our success in accomplishing this task that our civilization will be judged by future generations.

I am not pronouncing any new doctrine. I am only placing special emphasis on it. All through history, our great religious teachers, our great philosophers, our great statesmen and generals have taught this lesson; but, to my knowledge, no conscious effort has been made towards its accomplishment. In medieval Europe, the most promising apprentices became the sons-in-law, and consequently partners, of their

employers. In the Far East, the Japanese adopted the most promising pupil as a child. Our modern civilization has painfully evolved an intellectual sausage machine, which, from heterogeneous raw materials, attempts to produce a uniform product, only distinguishable by the label attached by the manufacturer.

I could quote you pages of Faraday in a similar sense.

Let us consider now what steps we know to escape from this dilemma. The Continental Universities, following the tradition from the Middle Ages, have encouraged the migration of students, a process which, by natural selection, at least, permits the great pupil to come into the orbit of the great teacher.

The English Universities, by means of scholarships and fellowships, attempt to attract them (I won't say bribe), with a similar object. The North American Universities attempt to solve the problem with postgraduate Universities and research professorships. Perhaps the medical education in England, with its system of dressers and house physicians and surgeons, has most seriously attacked this problem.

My father, who felt most strongly on the subject, succeeded in persuading the London County Council to abolish examination for the Scientific Scholarship. A complex problem of this nature cannot be solved by a simple equation, especially as the solution is particularly difficult, since many of the attempts I have enumerated above are fundamentally vitiated by the system of examination, with its attendant educational malformation. Like so many other things, examination is a useful servant and a bad mistress, and when she gains the upper hand, she surrounds herself with a court of examiners, whose only economic *raison d'être* is that examinations serve to eke out the most inadequate remuneration we award to those to whom we entrust the scientific upbringing of our youth.

We shall have to provide opportunities where the young mind can develop untrammelled by any hard and fast system under the ægis of a wise and kind direction, and where every suitable aid to self-development and facilities for Scientific Research are amply provided.

In this connection, permit me to quote a review by Dr. John Davy of Sir Humphry Davy's ideals when President of the Royal Society :

" Whilst he was in office, the reputation of the Society was certainly not diminished, but rather exalted ; the desire to belong to it was increased ; its Transactions were scarcely at any former time more original or interesting ; and at no former period was there more harmony in the general body of the Fellows. And yet, I believe, my brother's expectations were not answered, and he effected very much less than he wished. Government was lukewarm or indifferent in matters of science, and gave him no effectual support ; when requiring the aids of science, and of the Fellows of the Royal Society, applying to him without hesitation, and, when their objects were attained, forgetting the services. It was his wish to have seen the Royal Society an efficient establishment for all the great practical purposes of science, similar to the college contemplated by Lord Bacon, and sketched in his New Atlantis : having subordinate to it the Royal Observatory at Greenwich, for astronomy ; the British Museum, for natural history, in its most extensive acceptation ; and a laboratory founded for chemical

investigation, amply provided with all means requisite for original inquiry, and extending the boundaries and the resources of this most important national science. I remember well his speaking to me more than once on the subject. He had even the idea of raising the funds necessary for forming a laboratory by subscription amongst the Fellows themselves, without the aid of government; and he probably would have attempted this and some other plans for the advancement of science, had his health remained firm. . . . "

This passage, from Davy's *Life and Work*, which stood on the bookshelf next to my father's writing table, may have originated the train of thought which, after much cogitation and deliberation, found its realization in the Davy-Faraday Research Laboratory. Acting as my father's amanuensis and assistant, and having been entrusted with the whole of the organization and installation, I well remember the many and serious discussions as to its scope, position and direction, so as to insure its fullest and most fruitful activity. The great friendship and admiration my father had for Sir James Dewar, my own first teacher (whom he had first met at the British Association Meeting at Ipswich), and the opportunity the Laboratory offered of improving both the accommodation of the Library, the Laboratories and Residential Quarters, was one of the factors which decided my father to connect the Laboratory with the Royal Institution. But the factor which finally decided us was the prestige and the success which this singular, semi-popular Institution (of which I am again proud to be Manager) possesses, in having succeeded to attract as its Professors, by some occult manner which savours almost of witchcraft, those who are greatest in Britain (I had nearly said England —which might have broken the spell).

This unbroken succession of great men gave my father the assurance that this well-established tradition would continue to flourish and that the wise direction of any institution entrusted to their care would be amply secured. Faraday had declined the Professorship of Chemistry at University College, fearing that the duties attached to that position would interfere with his liberty of research. It was to insure this very liberty that my father planned the Laboratory, and this emboldened him to name it after those two great ones whose widespread and fearless inquiries, perhaps better than in any other way, defined the scope of the Laboratory activities.

The Laboratory was opened in 1896 and 108 workers have published 218 papers, a large proportion in the *Philosophical Transactions* and in the *Proceedings* of the Royal Society. Many whose names are now well known have worked in its rooms; each one of which I installed, with the hope, since justified, that their arrangement would facilitate research. Before undertaking this, for me, momentous task of equipment, I visited many laboratories abroad, both in Europe and America, so as to secure the best and most suitable apparatus available. A most congenial task which brought me in close personal touch with many of the greatest researchers and their instrument-makers, and which I concluded with a well-spent week at the Physikalische Reichsanstalt, where I obtained most valuable assistance in ascertaining the most suitable of various types of instruments.

Considering the readiness with which Faraday placed his advice and experience at the disposal of all who sought it, I do not think there can be any doubt that Faraday would have both welcomed and co-operated in the foundation and conduct of this Laboratory.

I am convinced that both the late Director, Sir James Dewar, and the present distinguished Director, Sir William Bragg, would have, and that Sir William will bear me out in ascribing to the interaction of the minds and the atmosphere prevailing in a place devoted to pure research, much of the success and rapid progress of the workers and their work. Facilities, the best apparatus available, the services of a competent mechanic properly equipped, also contribute materially to this result ; but the spiritual impulse which defines questions, sharpens the power of observation, finds the solution of the problems and grasps the comprehension of the results, is stimulated by the all-pervading influence of those great minds who first penetrated and marked out the routes which lead us to an ever clearer understanding of the interaction of forces which surround us.

This clearer understanding leading to greater control, both of ourselves and of our surroundings, widens the sphere of human freedom with a corresponding increase in our well-being and the joy of life.

And in conclusion, having succeeded in finding and training our pupil, how can we best show him our appreciation and encouragement ? Let us again refer to Faraday's career.

His unselfish love of knowledge conquered the love and esteem of all his great contemporaries, who were proud to recognize him by electing him to ninety-five academic distinctions.

The Royal Institution could do no more than provide him with a congenial home and working facilities, but already Sir Robert Peel had desired and Lord Melbourne, succeeding him as Prime Minister, gave Faraday a Civil Pension in 1835, and subsequently, Queen Victoria gave him the use of a house at Hampton Court Green.   I mention this, not with the object of referring to the dignified and adequate manner in which Faraday dealt with a misunderstanding, partly of a political nature, in which the gift of this grant became involved ; but as an instance of how a century ago a question was treated, which has recently been submitted by the Committee of Intellectual Co-operation of the League of Nations, in regard to the recognition of those minds, whose Ideas have contributed to the benefit of mankind.   When considering this problem at the meeting of the Union of Pure and Applied Chemistry at Washington, I suggested that it was only on similar lines that this question could be dealt with, as any evaluation of ideas in terms of finance was an impossible and insoluble task.   Faraday's views of the recognition of science by the award of titles were expressed in a letter he wrote to Lord Wrottesley. I take leave to quote this letter as it deals with this question.

" My Lord,

" I feel unfit to give a deliberate opinion on the course it might be advisable for the Government to pursue if it were anxious to improve the position of science and its cultivators in our country. My course of life, and the circumstances which make it a happy one for me, are not those of persons who conform to the usages and habits of society.   Through the kindness of all, from my Sovereign downwards, I have that which supplies all my need ; and in respect of honours, I have, as a scientific man, received from foreign countries and Sovereigns, those which, belonging to very limited and select classes, surpass in my opinion anything that it is in the power of my own to bestow.

" I cannot say that I have not valued such distinctions ; on the contrary, I esteem them very highly, but I do not think I have ever worked for or sought after them.   Even were such to be now created here, the time is past when these would possess any attraction for me ; and you will see therefore how unfit I am, upon the strength of any personal motive of feeling, to judge of what might be influential upon the minds of others.   Nevertheless, I will make one or two remarks which have often occurred to my mind.

" Without thinking of the effect it might have upon distinguished men of science, or upon the minds of those, who stimulated to exertion, might become distinguished, I do not think that a Government should for its own sake, honour the men who do honour and service to the country.   I refer now to honours only, not to beneficial rewards ; of such honours I think there are none. Knighthoods and baronetcies are sometimes conferred with such intentions, but I think them utterly unfit for that purpose.   Instead of conferring distinction, they confound the man who is one of twenty, or perhaps fifty, with hundreds of others.   They depress rather than exalt him, for they tend to lower the especial distinction of mind to the commonplaces of society.   An intelligent country ought to recognize the scientific men among its people as a class. If honours are conferred upon eminence in any class, as that of the law or the army, they should be in this also.   The aristocracy of the class should have other distinctions than those of lowly and highborn, rich and poor, yet they should be such as to be worthy of those whom the Sovereign and the country should delight to honour, and, being rendered very desirable and even enviable in the eyes of the aristocracy by birth, should be unattainable except to that of science.   Thus much I think the Government and the country ought to do, for their own sake and the good of science, more than for the sake of the men who might be thought worthy of such distinction.   The latter have attained to their fit place, whether the community at large recognize it or not.

" But besides that, and as a matter of reward and encouragement to those who have not yet risen to great distinction, I think the Government should, in the very many cases which come before it having a relation to scientific knowledge, employ men who pursue science, provided they are also men of business.   This is perhaps now done to some extent, but to nothing like the degree which is practicable with advantages to all parties.   The right means cannot have occurred to a Government which has not yet learned to approach and distinguish the class as a whole.

" At the same time, I am free to confess that I am unable to advise how that which I think should be may come to pass.   I believe I have written the expression of feelings rather than the conclusions of judgment, and I would wish your lordship to consider this letter as private rather than as one addressed to the chairman of a committee. . . . "

How much further can we go ?
I have referred to Research Professorships, Fellow and Scholarships. Italy elects its most distinguished men of Science to the Senate, Germany makes them Privy Councillors.   We have since created the Order of Merit and Sweden Nobel Prizes, but should we not learn from

Queen Victoria and her Prime Ministers how to manifest national gratitude both in an honourable and substantial fashion ?

We require Faraday's inspiration even more in the future than we have done in the past. I have attempted to analyse the conditions which gave us a Michael Faraday. Let us endeavour, by recreating these conditions and atmospheres, to ensure that such individualities, as and when they do arise, may continue to develop and fructify.

PHOTOCHEMICAL PROCESSES.

A GENERAL DISCUSSION.

THE FIFTY-FIFTH GENERAL DISCUSSION organised by the FARADAY SOCIETY was devoted to "PHOTOCHEMICAL PROCESS," and served in part as an opportunity for reviewing the progress which had been made since photochemistry was first discussed by the Society at Oxford in October, 1925.[1]

The meeting was held in the University of Liverpool on the 17th and 18th April, 1931, the President of the Society (Dr. Robert L. Mond) occupying the chair.

The programme was divided into four parts, as follows :—

Part I. Molecular Spectra in Relation to Photochemical Change, which occupied the morning of the first day, was introduced by Professor R. Mecke, *Heidelberg.*

Part II. Photochemical Kinetics in Gaseous Systems was discussed during the first afternoon and the introductory survey was given by Professor Max Bodenstein, *Berlin.*

Part III. Photochemical Change in Liquids and Solids formed the subject of discussion during the morning of the second day and was introduced by Professor A. Berthoud, *Neuchâtel.*

Part IV. Photosynthesis was opened by Professor E. C. C. Baly, *Liverpool,* and was discussed during the afternoon of the second day.

The social headquarters of the meeting were at the Adelphi Hotel, where the President and Mrs. Mond on Thursday evening, 16th April, entertained to dinner the overseas guests and those from the British Isles who had come to Liverpool to take part in the meeting.

The President on behalf of the Society welcomed more especially his overseas guests. They were : Professor A. Berthoud (*Neuchâtel*), Professor M. Bodenstein (*Berlin*) who had just retired from the office of President of the *Deutsche Bunsen-Gesellschaft*, Professor J. Eggert, *Leipzig*, Dr. E. Falcké, *Leipzig*, Dr. W. Frankenburger, *Ludwigshafen a. Rh.*, Dr. Kondo, *Japan*, Dr. Lochte-Holtgrevin, *Gröningen*, Professor R. Mecke, *Heidelberg*, and Professor Otto Warburg and Frau Meyer-Viol, *Berlin.*

Dinner was taken on Friday evening at the University Club. Both of these functions provided the opportunity for making and for cementing friendships between the many workers on photochemistry who met under such pleasant conditions.

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[1] "Photochemical Reactions in Liquids and Gases," *Trans. Faraday Soc.*, **21**, 437, 1925.

At the conclusion of the morning session on 18th April, a photograph of those then present was taken in the quadrangle of the University. A reproduction of this photograph faces this page.

Those seated in the front row (reading from left to right) are Dr. Kondo, Professor Baly, Professor Berthoud, Mr. Emile Mond, Professor Bodenstein, the President, Professor Mecke, Sir Robert Robertson, Miss Wallace, Dr. Frankenburger, Professor Eggert, and Professor Allmand.

There will also be seen seated on the ground Messrs. Batley, McMillan, Eltenten, Leathwood, Williams, Belton, and Childs.

First row standing, Messrs. Kirkbride, Griffith, Willey, MacDonald, and Norrish, Mrs. Kerridge, Major Freeth, Professors Donnan, Spencer, and Porter, and Dr. Lochte-Holtgreven.

Second row standing, Messrs. Emeleus, Griffiths, Marlow, Childs, Style, Topley, and Bailey, Professor Partington, and Dr. Ludlam.

Third row standing, Messrs. Angus, Cassie, Smith, Stein, and Goodeve.

Copies may be purchased from Messrs. Medrington's Ltd., 29 Bolt Street, Liverpool.

At the conclusion of the meeting the thanks of those present were accorded with acclamation, at the instance of the President, to those who had come from overseas to contribute to the discussion Professor Bodenstein, in reply, congratulated the President on the success of the meeting, and on behalf of his fellow guests thanked him and Mrs. Mond for their hospitality.

Votes of thanks were also accorded with great cordiality to others who had contributed papers and had taken part in the Discussion, to the University and particularly to Professor Baly for hospitality, to the University Club, and to the Organising Committee (Professor A. W. Porter, Professor Allmand, Professor Baly, Dr. Griffith and Dr. Norrish).
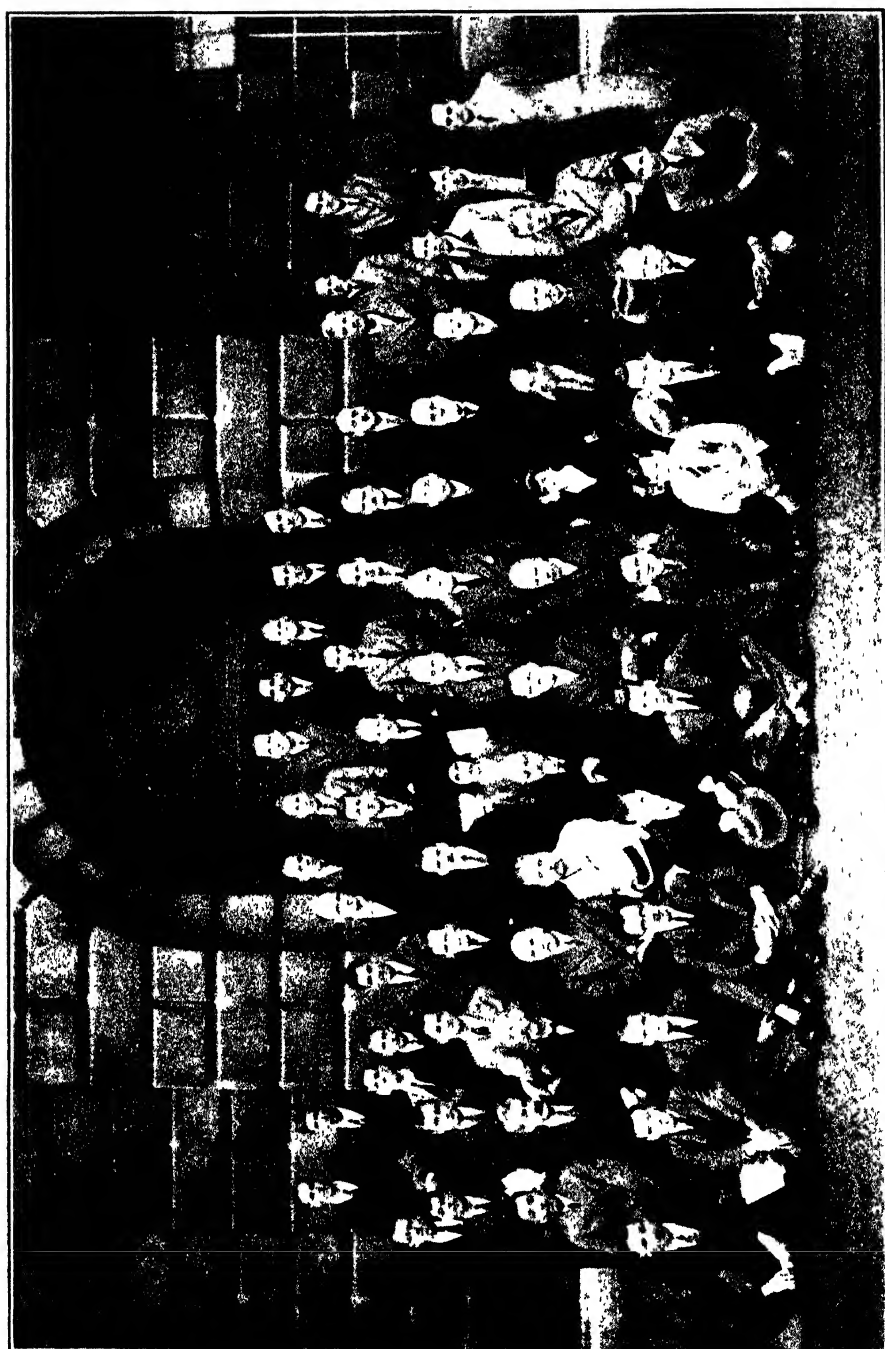
PHOTOCHEMICAL PROCESSES.

A GENERAL DISCUSSION.

PART I.—MOLECULAR SPECTRA IN RELATION TO PHOTO-CHEMICAL CHANGE.

Introductory Paper.

By Professor R. Mecke (*Heidelberg*).

Photochemical processes have already been a subject for discussion by the Faraday Society[1] (Oxford, October, 1925). At that time interest was centred mainly on the "Stark-Einstein law of equivalence," and it was one of the tasks of the meeting to decide how far its validity could be considered to be experimentally supported. Perhaps the most important result of the Discussion and of the papers contributed to this meeting is the fact that to-day opinion inclines to the view that for the primary reaction, although for this alone, the law is rigidly obeyed, *i.e.* "that each absorbed quantum $h\nu$ puts one, but only one, molecule into such a state that it is able to react." Should a photochemical efficiency greater or smaller than 1 be found—and that is the case with most reactions—the tendency to-day is not to question the Stark-Einstein expression, but, rather, to suggest that a very careful investigation is required as to the secondary reactions to which this result may be attributed. The number of possibilities for such reactions is as a rule large, and it is by reason of this fact that no small part of our present difficulty arises, as the numerous papers which have appeared on this subject since the Oxford meeting bear witness. The growing literature is also testimony to the great interest which is being increasingly shown in this branch of reaction chemistry, and the decision of the Faraday Society to place the topic once more under discussion comes at an especially welcome moment. From what has already been said it is clear that the orientation of the present meeting will be somewhat different from that taken up at Oxford, and may in fact be conveniently embodied in the following two fundamental questions which we have to answer.—

(1) How is it possible that an almost sluggish non-reacting molecule can be brought, by absorption of a certain light quantum $h\nu$, into an active state? (Part I.).

(2) Into what further reactions can such an activated molecule enter if it is in the gaseous phase (Part II.) or if it is in the liquid or solid phases (Part III.).

I propose to devote my attention mainly to question (1) and as briefly as possible to set forth what, from a *spectroscopic* point of view, are the conditions which must be fulfilled in order that a photochemical change can take place. It is not difficult to put forward general rules. The first necessary

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[1] *Trans. Far. Soc.*, **21**, 1925 (*Z. physik. Chem.*, **120**, 1926).

condition is, of course, that light be absorbed. Moreover, the Einstein expression $E = h\nu$ requires that the absorbed quantum should contain the energy-equivalence of the heat of reaction (activation) of the primary reaction. We expect, therefore, in all cases where non-monochromatic light is used, that there should appear in the absorption spectrum a somewhat sharply defined *long wavelength threshold* at which the reaction first begins to take place. The accurate determination of this threshold wavelength is of fundamental importance for a proper understanding of the primary reaction, but unfortunately it presents experimental difficulties. It sometimes happens, too, that the threshold cannot be found by reason of a cessation of molecular absorption in that particular region. The reaction will start once again, however, if molecules are added which *do* absorb in that region, and in this case we have the so-called "sensitised photochemical reaction" of which we know to-day many examples. It is only when we are absolutely sure that, in spite of ample absorption, the reaction ceases to take place, that we can with certainty identify this threshold energetically with the heat of activation. The existence of such a threshold is not, however, the only spectroscopic characteristic of a photochemical reaction. We know from experience that a molecule must be excited by absorption to an activated state of a special kind before conditions favourable for reaction can exist, and a still further necessity is that these activated molecules must be brought into contact with a sufficient number of other molecules which are susceptible to reaction; for a strictly monomolecular reaction that affects *only* the molecule by which light has been absorbed, is quite a rarity. The type of reaction which follows is frequently indicated by the value of the photochemical efficiency (*i.e.* the number of changed molecules per $h\nu$) since the numerical value of this quantum efficiency is mostly controlled by the number, kind and succession of secondary reactions. Values as high as $10^6 - 10^9$ are possible (chain reactions), and values smaller than 1 are not ruled out, if disturbing processes remove an appreciable number of the activated molecules before they are able to react.

In this part of the discussion we are primarily interested in the question as to the peculiarity by which the "activated" state of the molecule is distinguished, in order that it may give rise to a photochemical reaction. The now well-known facts of the sensitised photochemical reaction lead us to recognise two separate cases :—

(1) The absorption may bring about only simple *activation* (*i.e.* excitation of higher energy levels in the sense of Bohr's theory) and these activated molecules with their surplus energy play only the part of middlemen in the energy exchange (*cf.* the case of sensitised reactions) or have another structure more suitable for reaction or are decomposed by secondary reactions.

(2) A genuine photochemical *decomposition* can occur, in which case the molecule is split by the act of absorption into fragments which do not recombine, but which unite with other molecules to form quite new compounds.

There are now examples in plenty of both cases,[2] so that we may take them as proved and ask ourselves, "By what characteristics may we distinguish between those cases of merely molecular *excitation* and those of real molecular *dissociation* by light absorption?" In the following dis-

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[2] The idea of a primary decomposition process may perhaps be traced back to the work of Warburg on the photochemical decomposition of HBr and HI; whilst the excitation theory for these reactions is found in researches of Stern und Vollmer (*Z. wiss. Photogr.*, **19**, 275, 1926).

cussion I am compelled through force of circumstances to limit myself chiefly to gaseous reactions; it is mostly for these that we can make use of the knowledge gained in recent years from the study of band spectra, in order to follow the absorption process in all its details.

1. Photochemical Reactions with "Activated" (Excited) Molecules.

Coming next to the question as to what goes on in a molecular gas during the absorption of light, I need only briefly mention that molecular energy contains three components—rotational, vibrational and electronic energy—and that according to Bohr the frequency of an absorbed or emitted spectral line is determined by *change* of this molecular energy. Should only the rotational energy change, then we have the so-called rotation spectra in the far infra-red ($> 20 - 30 \mu$). Photochemical processes depending only on an alternation of rotational energy will never be observed under ordinary circumstances—even if it be admitted that they are possible—since the energy ($< 1\cdot5$ Cal.) corresponding to such wavelengths is of the same order of magnitude as ordinary thermal energy. Nor can an alternation of the vibrational energy bring about a photochemical reaction, since such a change is wanting in important properties (about which I will say more later) which an activated (*i.e.* excited) molecule must possess. We have thus arrived spectroscopically at our first conclusion, "that only a *change of electronic energy* (which may but need not necessarily cause decomposition) is required to bring about a photochemical reaction." Experience has shown that at least in gases the energy required to produce an alternation in the electron configuration is almost always greater than $25 - 30$ Cal. ($< 1 \mu$), so that from purely spectroscopical reasons we can state the well-known fact, that only visible or ultra-violet light is photochemical active.

We can distinguish yet a second necessary criterion for bringing about a photochemical reaction, namely, the *loss of the power of fluorescence* of the molecule. A simple well-known example will serve to illustrate my meaning. Suppose we take a strongly fluorescent gas (Hg or I_2 vapours) and with this mix an inert gas (He, A, N_2) then with increasing partial pressure of the inert gas the fluorescence is gradually extinguished. The explanation is readily ascertained. The molecule or atom is elevated by absorption to a higher, excited, energy level from which it returns—after a mean life of something like 10^{-8} seconds in attenuated gases—to the ground state by re-radiating its energy. If, however, the time between successive impacts with neighbouring molecules is of the same order as the mean life in the excited state, then the re-radiating process (*i.e.* fluorescing power) will be disturbed, and the degree of disturbance will depend on the pressure and the nature of the gas. In this case the energy of excitation will be converted into thermal energy. But should a potentially active gas (H_2, O_2, Cl_2) be chosen in place of an inert gas, and should, of course, the energy communicated be large enough, then a photochemical reaction occurs. We see then an obvious characteristic of such reactions, with excited molecules with the mean life of 10^{-8} secs. in the partial extinction of the fluorescence, and further we can draw the conclusion, "that with such reactions the quantum efficiency will as a rule be small (< 1) and very sensitive to pressure, *i.e.* the primary reaction is bimolecular (two-body collisions) or even termolecular (three-body collisions)."

The only exception to this rule arises when the primary process of absorption can set up a chain reaction with its attendant high efficiency.

Some relevant examples can be seen in the photosynthesis of HCl from H_2 and Cl_2, and in the reaction $2H_2 + O_2 = 2H_2O$. It is of course necessary that the energy required by the heat of activation of the *primary* reaction be present. In the case of HCl formation it is the energy necessary to form Cl atoms (57 Cal.) and for the H_2O reaction to form O atoms (118 Cal.) from the molecules.[3] As soon as this condition is fulfilled each short lived excited molecule can bring about the reaction.

It is possible to put this dependency on pressure into a simple formula. We will call γ the quantum efficiency of the primary process, *i.e.* the number of excited molecules which, for each absorbed quantum $h\nu$ will react with the molecules $[M]$ (maximum $= 1$). Further let $k[M]$ be the number of effective collisions per second which will lead to this reaction and τ the mean life of the excited molecule after which it will return to the ground state either by fluorescence or by ineffective collisions. Then this quantum efficiency of the primary reaction will be

$$\gamma = \frac{(\tau k)[M]}{1 + (\tau k)[M]}.$$

Now it might happen that at ordinary pressure the mean life and the number of effective collisions are sufficiently large $(\tau k)[M] \gg 1$ to ensure that practically all the excited molecules will react, and thus the efficiency turns out to be 1. By lowering the pressure, however, the efficiency will always decrease, at first very slowly, afterwards rapidly, becoming at least proportional to $(\tau k)[M]$.

Let us now change this formula a little for the case of an active gas diluted by some inert gases. For this purpose we will introduce the mean life of an excited molecule in a highly attenuated gas, *i.e.* the time after which it will return to the ground level *only* by light emission : τ_0. Let c be the total number of collisions (effective and ineffective) which remove the excited molecules and $[p]$ the total pressure of the gas ; then the formula will become

$$\gamma = \frac{(\tau_0 k)[M]}{1 + (\tau_0 c)[p]}.$$

Here the quantum efficiency of the primary reaction will always be smaller than one. But in any case we see that there are two possibilities of *increasing* this quantum yield : (i) by raising the mean life τ_0 of the excited molecule and (ii) by raising k, the effective cross section of the reacting molecules. We have to ask whether this is possible, and indeed it is.

In addition to the short-lived class of states we know spectroscopically of still another class with a mean life of $10^{-2} - 10^1$ seconds, the so-called "metastable" atoms or molecules. Owing to their long life they can survive a large number of collisions with other molecules or atoms. Fluorescence (*i.e.* radiative transition to the ground state) occurs with this class only under extreme conditions (*very* low pressure), since these transitions are inhibited on account of the long life of the excited state. With non-fluorescing molecules such as these, we can always improve the photochemical efficiency nearly up to its theoretical value 1, assuming of course that we are in a position to produce these molecules quite easily. The classic example is

[3] If hydrogen atoms could start the chain reaction, a mixture of H_2 and O_2 sensitised by mercury vapour would explode in the light of a mercury lamp ($\lambda 2536$), but what really happens is the formation of hydrogen peroxide according to the scheme $2H + O_2 = H_2O_2$ (*e.g.* A. L. Marshall, *J. physical Chem.*, **30**, 1078, 1926, or K. F. Bonhoeffer and S. Loeb, *Z. physik. Chem.*, **119**, 474, 1926).

mercury vapour.   By radiation with $\lambda 2536$, mercury vapour can be brought from the ^1S ground level to the $^3P_1$ state.   Immediately under the $^3P_1$ level, and therefore easily to be reached from it through collision with other Hg atoms or foreign gases (N_2), is the metastable $^3P_0$ state (corresponding to · $\lambda 2656$).   A return from this to the ground state by radiation is hardly probable.   Should, therefore, the foregoing process really be instigated by radiating with $\lambda 2536$ (from the so-called mercury resonance lamp), it would be difficult to imagine conditions better suited to bring about a transference of 107 Cal./mol. by impacts.   Probably the best known case in which use is made of mercury sensitising is the photochemical production of hydrogen atoms by Cario and Franck.[4]   Whether this decomposition of the hydrogen molecule (101 Cal.) follows directly by impact—

$$Hg' + H_2 = Hg + H + H + 6 \text{ Cal.}$$
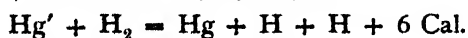
or is a consequence of a secondary reaction—

$$Hg' + H_2 = HgH + H + 14 \text{ Cal.}$$

(as suggested by Compton[5] and later followed up by Gaviola and Wood,[6] and Beutler and Rabinowitsch,[7] and proved by the appearance of HgH bands in the spectrum) is of minor importance.   The main point is the existence immediately under $^3P_1$ $(\lambda 2536)$ of a metastable level which makes it possible to produce energy charged atoms and with them to *raise* the photochemical efficiency.   Mercury vapour is also an important sensitiser for reactions other than that quoted above (*e.g.* in the photochemical decomposition of hydrocarbons, or water according to—

$$Hg' + H_2O = HgH + HO + 2 \text{ Cal.});$$
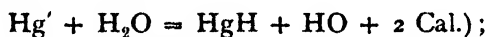
it is only necessary that the heat of reaction shall be less than 107 Cal., or in the case of HgH formation less than 115 Cal., in order that the threshold shall be well covered.   Neither oxygen nor methane should very readily be decomposed by such photochemical means, as the atoms are too tightly bound for the energy at our disposal (O_2 118 Cal., $CH_4 \sim$ 115 Cal.).[8]   At any rate the need for caution is apparent when the photo-reactions of gases contaminated by mercury vapour are investigated with the mercury lamp.

Molecules can also possess metastable states.   Here the best example is active nitrogen,[9] which after being formed from nitrogen atoms is left in a metastable state carrying an energy of about 190 Cal. and one bond split up : $\overset{\cdot}{N} = \overset{\cdot}{N}$.   Its reactivity is thus easily understandable, although for genuine photochemical reactions it is of little use owing to the unfavourable spectral region (λ 1500).   Hydrogen possesses a similar high-energy metastable state ($^3\Sigma = 270$ Cal. $\lambda 1050$) which is, however, also of lesser importance, since active hydrogen *atoms* are obtained with far less energy (101 Cal.) from other sources.   To the list of *known* metastable molecules I would add "active" oxygen as a new one with extraordinarily low excitation energy.   The transition from the ground state is well known to give rise to the weak atmospheric oxygen bands ($^3\Sigma \rightarrow {}^1\Sigma$).   We were able recently to estimate the mean life of this $^1\Sigma$ state and find a value[10]

[4] G. Cario and J. Franck, *Z. Physik*, **11**, 161, 1922.
[5] K. T. Compton and L. A. Turner, *Phil. Mag.*, **48**, 360, 1924.
[6] E. Gaviola and R. W. Wood, *Phil. Mag.*, **6**, 1191, 1928.
[7] H. Beutler and E. Rabinowitsch, *Z. physik. Chem.*, **8**, 403, 1930.
[8] R. Mecke, *Z. physik. Chem.*, **B7**, 121, 1930 ; *Z. Elektrochem.*, 589, 1930.
[9] Discovered by E. P. Lewis (*Astr. J.*, **12**, 8, 1900) thoroughly investigated by Lord Rayleigh and many others, last paper, *e.g.* Z. Bay & W. Steiner (*Z. physik. Chem.*, **B, 9,** 93, 1930).
[10] W. H. J. Childs and R. Mecke, *Z. Physik*, **68**, 344, 1931.

of about 7 secs. Since the bands lie at $\lambda 7600$, about the long wave limit of the photochemically active region, we must assume that active oxygen is capable of setting up reactions with a small heat of reaction less than 37 Cal. Such a reaction is, *e.g.*, the decomposition of ozone, so that "active" oxygen may well play an important part in the ultra-violet ozone formation and decomposition which goes on in the upper atmosphere.[11]

The other method of increasing the quantum yield of a photochemical reaction (raising k) is possible by some peculiar "resonance" phenomena. It has repeatedly been found from experiment that the probability of transferring energies by impact is the greater, the smaller the amount of energy which has to be taken from or put into translational energy (= non-quantised energy). Or speaking chemically : "the smaller the heat of reaction by impact the larger the efficiency.[12] As an example we can take a mixture of sodium and mercury vapour.[13] This mixture, when irradiated with a mercury lamp ($\lambda 2536$) emits by the so-called "sensitised fluorescence"[14] the sodium doublet $\lambda\lambda 4423/4420$ $(7^2S - 2^2P)$ with a quite unusual intensity in the ordinary excited line spectrum of sodium, since the energy of the photochemically excited $^3P_1$-mercury atoms is approximately the same as that necessary to excite the sodium atom to the 7^2S state $(1^2S - 7^2S)$. By mixing N_2 with the vapours, we can bring a considerable number of $^3P_1$ mercury atoms into the metastable $^3P_0$ state, for N_2 can take up very easily the surplus energy of the mercury atoms as vibrational and rotational energy. Instead of the doublet $\lambda\lambda 4423/4420$ the doublet $\lambda\lambda 4752/4748$ $(5^2S - 2^2P)$ will now appear more intense, since the energy of the $^3P_0$ mercury atom is approximately the same as that of the 5^2S sodium atom. Many of the striking fluorescence phenomena of active nitrogen may be explained by this resonance effect in the energy transference. In all these cases the energy transferred by impact is utilised again in the emission of spectral lines (a very sensitive test for resonance effects), but it could equally well have been utilised in increasing the yield of a photochemical reaction. I have already mentioned the quite similar cases of the production of H atoms and the dissociation of water vapour by sensitised Hg reactions ; but I have unfortunately no space to go into all the details of these interesting reactions. I will mention only the case of ozone formation in ultra-violet light, which does not seem to have been dealt with till now. As we shall see later, only *excited* oxygen molecules are responsible for the formation of ozone. The line $\lambda 1850$ is the only one from the mercury lamp strongly absorbed by oxygen and is for this reason chemically active. Excited O_2 molecules produced in this way possess sufficient energy to dissociate by impact the normal molecules (= 118 Cal.), and at the same time to fall, themselves, into the already mentioned $^1\Sigma$ metastable state with no energy surplus. Thus $O_2'' + O_2$ $= O_2' (^1\Sigma) + 2O$. The secondary reaction would then be $O + O_2$ $= O_3 + 27$ Cal. Another possibility is, below $\lambda 2020$, the formation of ozone directly and of one metastable oxygen atom : $O_2'' + O_2 = O_3 + O$ (^1D). This scheme explains readily the high efficiency of ozone formation

[11] R. Mecke, will appear in *Z. physik. Chem.*, 1931 ; Decomposition by red light *v.* H. J. Schuhmacher, *J. Amer. Chem. Soc.*, 52, 2377, 1930 ; Riesenfeld and Wassmuth, *Z. physik. Chem.*, B 8, 314, 1930.

[12] If there is a large amount of surplus energy, three bodies collisions are necessary to take it up.

[13] H. Beutler and B. Josephy, *Z. Physik*, 53, 747, 1929 ; L. Nordheim, *Z. Physik*, 36, 496, 1926.

[14] G. Cario and J. Franck, *Z. Physik*, 17, 202, 1926.

by excited molecules; the formation of ozone in the atmosphere follows no doubt on quite similar lines. Summarising now, we can say, "The photochemical excitation theory is under the usual conditions of excitation only applicable to those cases of usually small quantum efficiency which are strongly dependent on pressure (excluding chain reactions). The larger efficiencies are bound up with some resonance effects and with the existence of metastable states, which optically can only be attained indirectly from neighbouring states by resonance impacts or reactions." Which of these two factors—the resonance effect or the metastability—will give the greater quantum yield cannot be said at once. At any rate there will never be a quantum yield 1, as a part of the energy to be transferred will always be lost as thermal energy.

The thresholds and the heats of reaction placed at our disposal by the known metastable states of the common gases O_2, N_2, H_2 and Hg are shown in Table I., together with the energies necessary to decompose these molecules.

TABLE I.

		O_2.	N_2.	H_2.	H_2O.	Hg.		
Metastable energy	λ Cal.	7600 37	1500 190	1050 270	— —	2656 107	(2536) 112	(1850) 154
Dissociation energy	λ Cal.	2470 118	1350 210	2800 101	2550 112	— —	— —	— —

Whether or not other molecules (*e.g.*, the halogens) possess favourably situated metastable levels, or whether similar arguments are applicable also to the liquid and solid phases are questions which at this juncture we are not in a position to answer. But from the facts presented here we see, at any rate, that the excitation theory with its great variety of possibilities * merits very careful investigation and that the case of the mercury sensitiser is the only one known to us in spectroscopic detail.

2. Photochemical Reactions with "Primary Dissociated" Molecules.

Under certain experimentally proved conditions it is possible that the act of absorption instead of producing an excited state leads to direct dissociation of the molecule. This possibility of obtaining heats of dissociation spectroscopically from the value of the dissociation threshold is at once apparent and has of course long been realised, in fact as early as 1917 Trautz [16] wrote: „ Die Aktivierungswärme lässt sich als ein Produkt $\left(\dfrac{Rh}{k}\right)\nu$ auffassen, worin ν die im Spektrum tiefstliegende Eigenschwingung der Reaktion ist. Diese Eigenschwingung lässt sich im Spektrum der reagierenden Stoffe wiederfinden und so lassen sich Aktivierungswärmen und Wärmetönungen spektroskopisch bestimmen, sobald man Kriterien hat für die Auswahl der Schwingungszahlen." The criterion for these— still in use to-day—was also suggested, taking chlorine as an example: „ Wählt man nicht den Beginn des Linienspektrums (he refers to the lines

[16] M. Trautz, *Z. anorg. Chem.*, 102, 120, 1917.

of the band spectrum) sondern $465\mu\mu$, den Beginn des kontinuierlichen Absorptionsbands, das weit ins Ultraviolett reicht, so kommt man zu der Zerfallswärme des Chlors spektroskopisch berechnet = 61136 cal." Later the significance of spectroscopic threshold frequencies was recognised by the statement : „ Man kann Aktivierungswärmen und mithin auch Wärmetönungen bestimmen durch Ermittlung der längstwelligen photochemischen Empfindlichkeitsmaxima. Diese wieder können aus spektralen Messungen entnommen werden, wenn man Kriterien für ihre Auswahl unter den gemessenen Wellen besitzt. Diese Kriterien sind freilich heute noch nicht deutlich zu erkennen." These general criteria were lacking owing to the scarcity of spectroscopic information at that time, so that it was not until 1925 that Franck [16]—at the Faraday Society meeting at Oxford—could point to them with certainty in the absorption spectrum of iodine, which had been analysed by me [17] two years before. I venture to repeat these criteria here :

When following up a series of bands we find that they always converge to a limit, which is at the same time the starting point of a continuous absorption spectrum. This convergence point is identified with the threshold frequency for the primary dissociation of the molecule, so that the heat of dissociation can at once be easily calculated. I was able to fix the convergence limit for iodine quite accurately at $\lambda 4995$. That on the further side of this limit (*i.e.*, on the short wave-length side) the process of dissociation begins, has been shown by a number of widely different phenomena, both for iodine and for the similar case of hydrogen iodide (HI). Take for example the loss of the power of fluorescence. The strong fluorescence of iodine vapour which is produced by longer wave-length disappears at once as soon as the convergence limit is passed (Dymond).[18] We have here a criterion already proposed for a photochemical reaction. Bonhoeffer and Farkas [19] have shown that parallel with a marked increase of pressure (produced by the dissociation) there is an increase of chemical activity, made apparent by the so-called " cleaning up " effect. The existence of a dissociation is proved by Senftleben,[20] who found a change in thermal conductivity and finally spectroscopically by Turner [21] from the appearance of the atomic line spectrum. This last phenomenon—the appearance of an atomic line spectrum after irradiation of a molecular gas by nonmonochromatic light—has been further developed by Terenin [22] into still another method for determining heats of dissociation. Similar convergence limits are known for many other molecules (*e.g.*, Cl_2, Br_2, O_2, H_2). It is clear from what has been said that the photochemical dissociation of a molecule into atoms or groups of atoms is an experimental certainty. But we can go still further now and make the general statement, "That the appearance of a continuous, *i.e.* non-quantised absorption spectrum of a gas is always a sign of photochemical dissociation taking place in the gas."

It still remains to explain why in one spectrum (*e.g.*, the ultraviolet absorption spectrum of oxygen) the convergence limit is directly observed, whilst in another absorption spectrum of the same gas (*i.e.*, red absorption spectrum of O_2) it is missing. The explanation is due to Condon-Franck.

[16] J. Franck, *Trans. Far. Soc.*, **21**, 1925.
[17] R. Mecke, *Ann. Physik*, **71**, 104, 1923.
[18] E. G. Dymond, *Z. Physik*, **34**, 553, 1925.
[19] K. F. Bonhoeffer and L. Farkas, *Z. physik. Chem.*, **132**, 255, 1928.
[20] H. Senftleben, *Ann. Physik*, (5), **2**, 847, 1929.
[21] L. A. Turner, *Physical Rev.*, **27**, 397, 1926.
[22] A. Terenin, *Z. Physik*, **37**, 98, 1926.

In Fig. 1 the potential energy is plotted in the usual way as a function of the nuclear distance, the lower curve for the ground level and the upper curve for an excited state. We must next distinguish between three possible cases: (1) That through excitation, *i.e.*, a re-arrangement of the electrons in the molecule, the molecular binding forces will be *weakened*, (2) that they remain the same by this excitation process, and (3) that the molecule will be still more firmly bound together. The Condon-Franck theory postulates that the act of absorption is instantaneous compared with the time of vibration of the molecule, so that during absorption the nuclear distance remains appreciably unaltered. It is thus easy to imagine that— starting from a not too vigorously vibrating molecule in the ground state (this is the case with which we have to deal most in absorption)—the molecule after absorption possesses more energy than the dissociation energy of the excited state, case (1). On completing the vibration the
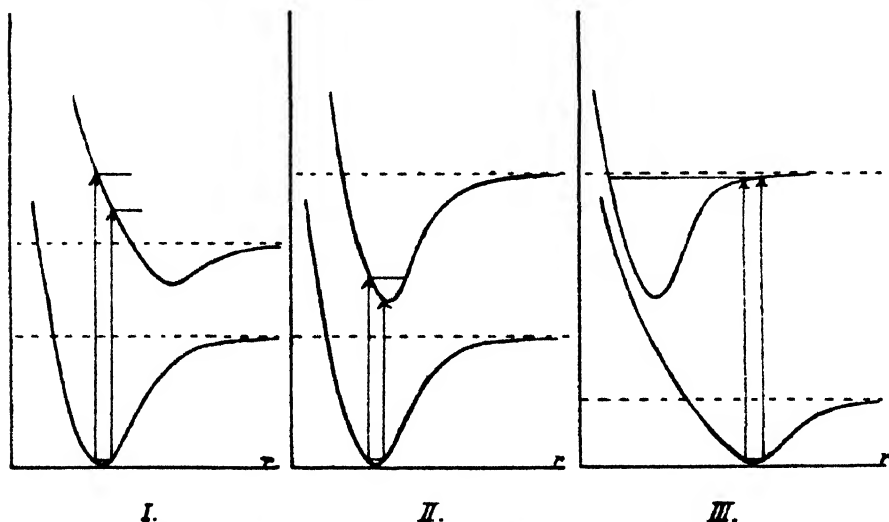
FIG. 1.—Potential Curves. I. Molecular bond weakened by excitation. II. Molecular bond unaltered. III. Molecular bond strengthened.

molecule will dissociate at once. A strengthening of the binding forces, case (3), can also (paradoxical though it seem) bring the molecule near to the point of dissociation. Only if the forces remain the same, case (2), do we obtain the usual quantised vibration spectrum. At any rate we are always able to impress on a molecule by electronic excitation a high amount of vibrational energy if only the binding forces are considerably altered by this process. In some cases it might happen that only this exaggerated amount of vibrational energy will start a photochemical reaction, although I think it is not very probable. Actually, convergence limits and continuous absorption have until now only been observed for those molecules in which the *binding forces are appreciably weakened by absorption.*

The extreme case of a continuous absorption spectrum without a neighbouring band spectrum and a convergence limit is also possible. I would especially mention the case of HI (investigated by Bonhoeffer and Steiner[23]) and some alkali metal halogen compounds. We must assume here that no *stable* excited state exists for these molecules (Fig. 2), so that

[23] K. F. Bonhoeffer and W. Steiner, *Z. physik. Chem.*, 122, 287, 1926.

on excitation dissociation takes place in any case. Photochemically this idea is well supported. If we assume the existence of excited molecules only, as Stern and Vollmer did for their theory of excited molecules, we have great difficulty in understanding the results of the very reliable measurements of Warburg, who found, even at low pressures, a total efficiency of two ($HI + h\nu = H + I$; $H + HI = H_2 + I$; $I + I = I_2$). For we thus conclude that a "complete quantum yield, *i.e.* a whole numbered efficiency practically independent of pressure (monomolecular primary reaction) is only to be explained by primarily dissociated molecules, a conclusion which may be contrasted with that drawn for the case of sensitised reactions."

As yet we have made no attempt to consider any questions as to the products of dissociation. The case which comes first to mind—that ordinary unexcited atoms or radicles are produced—is in practice seldom found. With the halogens, as Kuhn and Franck have shown, one normal ($^2P_{\frac{3}{2}}$) and one excited metastable atom ($^2P_{\frac{1}{2}}$) must result from dissociation. For this, naturally, more energy is required than for dissociation into two normal atoms and in order to obtain the energy of dissociation (as chemically defined) allowance has to be made for the extra energy which was required to excite the one atom, by subtracting it from the observed threshold frequency. It is not always easy to decide from the spectroscopic data the states of the products into which the molecules dissociate, although as a rule the number of possible states is not large.
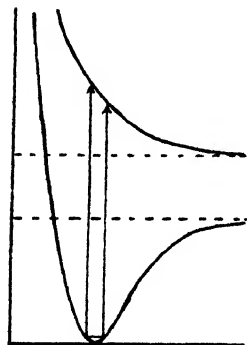
FIG. 2.—Continuous Absorption Spectrum.

I would like to take this opportunity to point out a possibility which does not seem to have been noticed as yet, and follows from the fact that the excited atom resulting from dissociation is very often in a metastable state. For example, irradiating oxygen with light of a wave length $<\lambda 1750$ produces one normal ^3P atom, and one metastable ^1D atom (excitation energy $= 45$ Cal.). It is easy to imagine many cases where this metastable atom *alone* is capable of furthering the reaction, since it possesses, in addition to its increased chemical activity as an atom, a surplus energy of 45 Cal. Thus there can exist a class of reactions with excited atoms produced directly by dissociation. It is desirable to investigate the question whether such reactions really are possible.

Cases in which normal atoms are the products of the absorption process are not known for band spectra with observed convergence limits. Only a few examples are known where the molecule absorbs continuously. In any case such dissociation is a rarity. From the phenomena which I have described we may perhaps be permitted to draw the following final conclusions :—

"On the short-wave side of the band convergence limit and in a spectral region distinguished by continuous absorption and by the fact that the molecules cease to fluoresce, a photochemical reaction with the theoretical quantum yield 1 can take place (chain reactions are of course excluded from this last statement). At the entrance to this region is a spectral region, more or less wide, in which the absorbed energy is *not* sufficient to produce primary dissociation, but which nevertheless is large enough, when transferred by impact, to produce dissociation by sensitising. In this

spectral region as is usual for reactions with excited molecules we obtain only a fraction of the theoretical yield per quantum (bimolecular primary reaction); as the convergence limit is approached, however, this yield rapidly attains the maximum value 1."

In Fig. 3 I have illustrated these ideas graphically, and for the common gases which have most frequently been used in photochemical investigations the spectroscopically obtained data are collected together in Table II. I have given the wavelengths of the observed convergence limits, the real reaction thresholds (= energy of dissociation into *normal* atoms) and the beginning of band absorption (= excitation energy of the molecule) since of course such absorbing molecules may be used in sensitised reactions. So far as I am aware, in all the cases in which halogens have been investigated, the
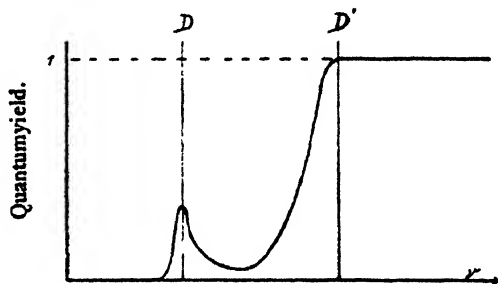
Res. bimolecular. Monomolecular.
Dissociation.
FIG. 3.—Diagrammatic representation of the quantum yield by "sensitised" and by "primary" dissociation.

light source was such that the primary dissociation could be considered as certain. On the other hand N_2 and CO must be regarded as photochemically inert gases, whilst with H_2, O_2 and H_2O, primary dissociation plays, in practice, no rôle at all. Of the photosensitised dissociation of these molecules I have already spoken. With water vapour, according to Leifson,[24] a continuous absorption spectrum begins at $\lambda 1390$ (204 Cal.)

TABLE II.

	Dissociation Energies Cal./Mol.		Limits of Sensitised Decomposition.	Photochemical Dissociation.	Beginning of Molecular Absorption.
	D	D'			
Cl_2	57·0	59·5	λ 5000	λ 4780	λ 5800
Br_2	45·2	55·6	λ 6300	λ 5100	λ 7600
I_2	35·2	56·8	λ 8050	λ 4995	λ 8000
HCl	101	103·5	λ 2800	λ 2740	λ 2700
HBr	85	95·5	λ 3350	λ 2970	λ 2900
HI	70	91·5	λ 4070	λ 3100	λ 3100
H_2O	112	204	λ 2550	λ 1390	λ 1800
H_2	101	335 (!)	λ 2800	λ 850	λ 1110
O_2	118	163	λ 2400	λ 1750	λ 2020
N_2	210	?	λ 1350	λ ?	λ 1450
CO	240	285 ?	λ 1200	λ 1000 ?	λ 1550

at the end of a series of bands. We have here obviously a case of a convergence limit with dissociation into a normal H-atom and an excited OH molecule (92 Cal.). We thus have the dissociation energy of water-vapour now measured thermally [25] (115 ± 5 Cal.), optically using Hg sensitising [26] (112 − 115 Cal.), and finally by the above convergence limit (112 Cal.) with some degree of certainty. I mention these facts here to show that the

[24] S. W. Leifson, *Astrophys. J.*, **63**, 73, 1926.
[25] K. F. Bonhoeffer and H. Reichardt, *Z. physik. Chem.*, **139**, 75, 1929.
[26] H. Senftleben and J. Rehren, *Z. Physik*, **37**, 529, 1926.

effect which is so often observed of moisture on photochemical reaction must be due principally to secondary effects (molecule + H_2O associations), and only very seldom to sensitised dissociation of water vapour into OH and H.

I cannot close this section without saying a few words about the oldest and most widely known of all photochemical reactions : the AgBr dissociation and the modern sensitising of the photographic plate. The foregoing discussion is of course not immediately applicable here, since we are dealing with the solid phase (crystal). However, one fact emerges from all the many experiments which have been performed, that "the primary reaction is the photochemical dissociation of AgBr into Ag and Br." The yield per quantum has also been determined with some degree of certainty as 1 (Eggert, Noddack). We are, therefore, justified in regarding the absorption spectrum of solid AgBr, which together with the photographic sensitivity begins rather sharply at λ4600, as a genuine case of a continuous dissociation spectrum. To explain the sensitising action of some dyestuffs it would then be natural to assume that this blue-violet absorption produces excited atoms by the primary dissociation and that dyeing the plate serves only the purpose of shifting by " sensitising " the absorption spectrum to the threshold of dissociation into normal atoms. Unfortunately this simple explanation, assuming a genuine sensitising process, does not seem to be the right one. It seems much more probable that the dyeing process produces real disturbances in the crystal surface of the silver-bromide grains, which materially reduce the amount of energy necessary to bring about dissociation. Spectroscopically the evidence points to this latter view, as do the facts that all the photographic sensitivity curves are very similar, with a steep long wavelength increase [27] to a maximum and a much more gradual decrease on the short wavelength side, and that the absorption spectra of the dyes do not at all agree with the sensitivity curve (this latter usually extends to much longer wavelengths). The case of desensitising a plate (corresponding to a strengthening of the binding forces) can also be made understandable. However, be that as it may, we are safe in regarding the primary process as a dissociation of AgBr into Ag and Br which later during the development process are able to set up a chain reaction. We see *in the photographic plate the very best example of a primary reaction (quantum yield 1) well separated from secondary reactions* (chain reactions of the development process, yield 10^9), and for this reason alone it would have been necessary to mention it.

3. Photochemical Reactions with " Pre-dissociated " Molecules.

So far, I have dealt only with diatomic molecules (with the exception of H_2O), for it is for these molecules alone that we have sufficient spectroscopic information to be certain about the details of the primary process. Polyatomic molecules, however, present a much more difficult problem and at present the knowledge we have of their excitation states, convergence limits, dissociation energies, etc., is very incomplete. It is fortunately sometimes possible to derive a good deal of information without knowing in detail the structure of the spectrum, by making use of a peculiar phenomenon discovered by Henri [28] and his co-workers and named by him " pre-dissociation ". The phenomenon consists in the sudden appearance

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[27] The Infra-red plates (neocyanine, rubrocyanine) with the farthest sensitivity to the red now known, have a steep drop of sensitivity near λ8800.

[28] V. Henri, " Structure des molécules," 1925.

in the jumble of bands in a spectral region—not very broad—where the line structure of the bands becomes blurred and diffuse : the bands are continuous. The phenomenon is plainly closely connected with some roots of dissociation process, but apparently with an incomplete dissociation, for we still see in the appearance of bands the vibrational quantisation and it is only the rotational quantisation of the molecule which has been disturbed. To understand this phenomenon it is important to remember that the period of a nuclear vibration is of the order $10^{-13} - 10^{-14}$ seconds, whilst that of rotation is some $10^{-11} - 10^{-12}$ seconds. These may be compared with the mean life of an excited electronic state : 10^{-8} seconds or still more. Bearing in mind these periods, we must assume, that the molecule during its existence in the excited state (10^{-8} sec.) is dissociated within *one* rotation, but not within the much shorter period of *one* vibration. Therefore, the case is only one of anomalous increased probability of the molecule to decompose and not one of direct dissociation such as we had in primary dissociation by absorption. To what specific cause this increased probability of dissociation must be attributed we are not yet quite sure, it seems, however, to be a resonance effect, probably with an unstable electronic level (see Fig. 4).[29]
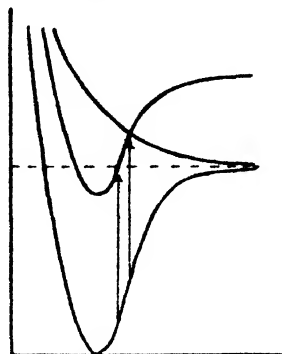
FIG. 4.—Predissociation.

A question which has especially to be solved, is whether this tendency to dissociate becomes marked first as soon as the dissociation energy is reached, or whether it begins only in the immediate neighbourhood of the intersection of the two potential curves (Fig. 4 shows only one possibility). The greatest dissociation probability occurs no doubt between these two limits. These regions of predissociation have been observed in the spectra of many polyatomic molecules, and some examples have been collected together in the Table which, however, does not

TABLE III.—PREDISSOCIATION.

Molecule.	Predissociation Observed.	Cal.	Probable Dissociation Products.	Energy Calc. from other Data.
NO_2	λ 3800 – 3700	75 – 77	NO + O	71 Cal.
	λ 2450	116	NO + O'	116
SO_2	$\sim \lambda$ 2500	$\sim$ 112	SO + O	$\sim$ 110
S_2	λ 2795	101	S + S	101
	λ 2590	109	S + S'	?
NH_3	$> \lambda$ 2260	$<$ 125	NH_2 + H	$\sim$ 90
H_2CO	λ 2670	107	HCO + H	$\sim$ 100
Cl_2CO	$\sim \lambda$ 2700	$\sim$ 100	ClCO + Cl	$\sim$ 80
$CH_3(HCO)$	λ 3050	95	? + H	$\sim$ 100
$C_6H_5(HCO)$	λ 2550	110	? + H	$\sim$ 100

pretend to be complete. The photochemistry caused by this increased tendency to dissociate is best illustrated by the case of NO_2 investigated photochemically especially well by Norrish,[30] and spectroscopically by

[29] G. Herzberg, *Z. Physik*, **61**, 604, 1930 ; R. de L. Kronig, *ibid.*, **50**, 347, 1928 ; **62**, 300, 1930
[30] R. G. W. Norrish, *J. Chem. Soc.*, 761, 1927 ; 1158, 1604, 1611, 1929.

Kondratjew, Herzberg,[31] and myself.[32]　　The spectroscopic data are as follows : The molecule (structure probably $O = N - O -$　) requires 71 Cal. to dissociate the first oxygen atom (single bond), but 150 Cal. for the second one (double bond).　Predissociation is observed between $\lambda 3700$ and $\lambda 3800$ (75-77 Cal.), and a second time at $\lambda 2450$ (116 Cal.) in a spectrum quite different from the first.　The first predissociation involves an energy slightly more than is necessary to split off the singly bound oxygen atom, the second predissociation corresponds directly to the energy required to get NO and an excited oxygen atom (O' ^1D).　The photochemical data observed by Norrish lead to exactly the same results : In spite of ample absorption (the absorption spectrum of NO_2 extends from $\lambda 7000$ to far in the ultra violet) the mercury lines $\lambda\lambda 5790$, 5770, $\lambda 5461$, $\lambda 4358$ have no effect at all.　The line $\lambda 4046$ (70·5 Cal.), consequent upon sensitised reactions with short-lived excited NO_2 molecules, shows a quantum yield of 0·74, but the theoretically expected value 2 ($NO_2 + h\nu = NO + O$, $NO_2 + O = NO + O_2$) is not obtained until the predissociation region is reached (obs. : 2·10 at $\lambda 3650$; 2·07 at $\lambda\lambda 3131 - 2967$).　Observation of the fluorescing power of the molecule yields the same information : where predissociation and a complete quantum yield are met with, a complete loss of fluorescence occurs.　From this quite typical example we see that predissociated molecules with a mean life much less than 10^{-9} seconds (normally the mean time between two successive collisions of a molecule) act photochemically in exactly the same manner as primarily dissociated molecules.

The behaviour of NO_2 is probably typical for a whole series of other predissociated molecules, and it would be really valuable if other photochemical reactions for which predissociation appears to be the cause could be investigated in the same extensive way, as has been done with NO_2. Only in this way can we hope to obtain informations reliable enough as to the real nature of predissociation, a phenomenon the details of which are as yet by no means clear.　I will mention here just one more example of predissociation where it had been possible to detect the dissociation products chemically.　The work of Bonhoeffer and Farkas[33] has proved that ammonia possesses a quite typical predissociation spectrum in the region below $\lambda 2200$, a region in which ammonia also is photochemically decomposible (Warburg).　Now when to a mixture of H_2 and O_2, heated almost up to the point at which explosion occurs, some ammonia vapour is added, explosion occurs at once on irradiation with suitable short-wave light,[34] because the H-atoms necessary for the propagation of the O_2-H_2-chain reaction have been provided by the predissociated NH_3 molecules. A heated mixture of O_2 and H_2 is evidently an extremely sensitive reagent for the detection of free H (and also O-　) atoms, which may prove very useful in the investigation of other "predissociated" molecules giving rise to these products.[35]

Summary

In this first part of my introduction, I have endeavoured to give a short review of the present situation of band spectroscopy so far as photochemical

[31] G. Herzberg, Z. physik. Chem., B10, 189, 1930 ; V. Kondratjew, Z. physik. Chem., B7, 70, 1930.

[32] R. Mecke, Naturw., 17, 996, 1929 ; Z. physik. Chem., B7, 108, 1929.

[33] K. F. Bonhoeffer and L. Farkas, Z. physik. Chem., 134, 337, 1927.

[34] L. Farkas, F. Haber and P. Harteck, Naturw., 18, 266, 1930.

[35] R. Mecke, Z. wiss. Photogr., 29, 72, 1930 ; H. J. Schuhmacher, J. Amer. Chem. Soc., 52, 2584, 1930.

reactions are concerned. I hope that I have been successful in demonstrating that, with a reasonably accurate knowledge of the absorption spectrum of the constituents, it should nowadays not be difficult to recognise the true primary process and find some indications as to its consequent secondary reactions. When at the same time the spectroscopic reaction threshold is also known the problem will be still more simplified. In conclusion I would like to present in a short summary the results to which I have come in these paragraphs.

We have learned that there are three possibilities for a photochemical reaction :—

(1) *Reactions with Excited Molecules.*—These can be recognised spectroscopically by the fact that the absorption spectrum is without any peculiarities in the appropriate spectral-region, *i.e.* with gases the spectra show the usual line structure and fluorescing power. Photochemically the primary reaction must proceed *bimolecularly*, with a quantum yield which, as a rule, is small and much dependent on pressure. Furthermore on adding substances which have an absorption spectrum corresponding to energies higher than the reaction threshold, the reaction remains the same (sensitised reaction).

The small quantum yield obtained by using short lived (10^{-8} sec.) excited molecules or atoms can be improved :

(*a*) By exciting *metastable* (long-lived) molecules or atoms, for which the return to the ground state by radiation is prevented precisely on account of their long mean life (10^{-2} – 10 sec.), so that the chances of successful impacts with reacting molecules are very much greater.

(*b*) By making use of *resonance effects, i.e.* by processes which proceed without heat of reaction (large effective cross-section). For these no " three-body collisions " are necessary to take up surplus energy.

Cases (*a*) and (*b*) can only be recognised by an extensive investigation of the band spectra and its energy relations.

(2) *Reactions with Primary Dissociated Molecules.*—Spectroscopically these can be recognised at once by the continuous spectrum (in the case of gases) and by the loss of fluorescence. Very often the continuous spectrum is preceded by an ordinary band spectrum with a convergence limit. Here the reaction can only occur under certain conditions as a " sensitised " reaction, namely when the products of the primary dissociation beyond the convergence limit belong to excited states. Photochemically the primary reaction in the continuous part of the spectrum proceeds as monomolecular and the quantum yield is complete and should be practically independent of pressure.

(3) *Reactions with Predissociated Molecules.*—These can be recognised spectroscopically by the sudden appearance, within a relatively small spectral region, by diffuseness in the band spectrum, combined with a loss of the power of *fluorescence.* The molecules concerned have only a greatly increased tendency to dissociation (mean life $\sim 10^{-11}$ sec.) and thus behave exactly as primarily dissociated molecules, from which they can only be distinguished by their peculiar spectrum.

I will now conclude my paper by saying a word or two about the papers contributed to this section of the meeting. Herzberg in his paper on the ultra-violet absorption of acetylene and formaldehyde investigates two compounds which, photochemically, merit special attention. In a paper in which I was able to determine the size and the fundamental frequencies of

this molecule,[36] I indicated that spectroscopically there must be a great similarity between C_2H_2 and N_2 and, I will add here, CO. If we adopt now the conception of Herzberg, that the ultra-violet absorption of C_2H_2 will correspond to that of N_2—and I have no doubt that it really does— we shall come to an understanding of some photochemical reactions. We now know [37] from comparison of spectra and from valence frequencies obtained by these that absorbing ultra-violet light by the N_2 molecule causes a partially splitting up of the threefold bond of $N \equiv N$, thus making the molecule reactional or active (N $=$ N). On the other hand we know that ordinary molecular oxygen has still two free valence electrons left unshared (O $=$ O), thus accounting for its high chemical activity. If we split up the valence bond of acetylene by ultra-violet absorption in the same way as can be done with nitrogen (HC $=$ CH) this excited molecule can associate directly with oxygen forming glyoxal and, after decomposition, formaldehyde or some other compounds :—

$$HC \equiv CH + h\nu \rightarrow (HC \bullet = \bullet CH)$$

$$HC \bullet = \bullet CH + O = O \mapsto HC = CH \rightarrow \begin{array}{c} H \\ \diagdown \\ O \end{array} C - C \begin{array}{c} H \\ \diagup \\ O \end{array} \rightarrow H_2CO + CO.$$
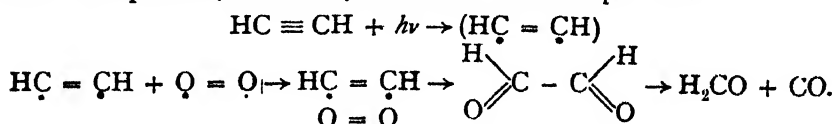
Many similar reactions of unsaturated compounds might be explained by this simple association reaction of *excited* molecules.

Coming to formaldehyde the similarity to oxygen, as stated by Herzberg, leads to the conclusion that ultra-violet absorption will split up the double bond of oxygen ($H_2C - O$) thus causing, by secondary reactions, the forma- tion of alcohols R(HCOH); organic acids R(HCOOH); or ethers R – O – R. But this synthesising reaction can be disturbed by a dissociation process. As Henri has found and Herzberg states again predissociation takes place at about $\lambda 2750$ (105 Cal.). I attributed [38] already this predissociation to a decomposition of formaldehyde in H + HCO requiring 105 Cal. This is of course according to Herzberg an upper limit of the dissociation energy. But chemical data have shown that the energy required to split off the first hydrogen atom from a hydrocarbon compound is above 95 Cal., mostly between 95 and 105. Assuming here a mean value of 100 Cal. I must state once more the fact that to dissociate the second hydrogen

$$(HCO \rightarrow H + CO)$$
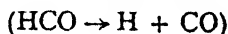
practically no energy at all is necessary, *i.e.*, formaldehyde dissociates by predissociation directly into hydrogen and carbon monoxide (= 103 Cal.). This seems to be confirmed, generally for all aldehydes, by the interesting paper of F. W. Kirkbride and R. G. W. Norrish, who show that the primary photochemical change is best represented by the scheme

$$R . HCO \rightarrow RH + CO.$$
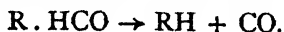
From this paper it seems very likely that the act of absorption will dissociate both atoms or radicles attached to the CO group in one step, or at least so quickly one after the other that it is more probable that they will combine with each other rather than with other atoms or radicles. It is thus obvious that a thorough spectroscopical investigation of these compounds

[36] K. Hedfeld, R. Mecke, *Z. Physik*, 64, 151, 1930; W. H. J. Childs, R. Mecke, *ibid.*, 64, 162, 1930; R. Mecke, *ibid.*, 64, 173, 1930; Levin and Meyer, *J. Opt. Soc. Am.*, 16, 137, 1928.

[37] R. Mecke, *Z. Elektrochem.*, 36, 589, 1930, and a coming paper.

[38] R. Mecke, *Nature*, April 5, 1930.

will reveal some more interesting features of the aldehydes as already shown in these two papers.

With regard to the paper of Goodeve and Stein, with whom I do not agree in regard to the explanation of the dissociation process and the molecular data used for this purpose, I want to make only a spectro-scopical remark. I have shown in this paper that the dissociation energy of water-vapour into H and HO is now well known (112) requiring a little more energy than is necessary to decompose OH (106 Cal.), thus showing again the well-known fact that the stable compound H_2O is more firmly bound than the unsaturated OH molecule. It has also been shown that the photochemical decomposition of water vapour can be raised by excited mercury atoms, the excitation energy of these atoms being practically the same (112). Applying these facts to the next compound of the oxygen group—H_2S—we find from spectroscopical data the dissociation energy of H_2S into H and SH to be about 87 Cal., this energy again being practically the same as that necessary to excite cadmium atoms to their first energy level (resonance line $\lambda 3261$), Cd having the same spectroscopic properties as Hg. Thus it would be very interesting to investigate the photochemical behaviour of H_2S sensitised by Cd-atoms (I do not think that, at low pressure without moisture, gaseous Cd will react chemically with H_2S), especially since HS is the only diatomic hydride compound up to Ca which spectrum is not known to us although there is no doubt that it will exist.

THE PHOTOCHEMICAL OZONE EQUILIBRIUM IN THE ATMOSPHERE.

By R. Mecke (*Heidelberg*).

The well-known fact that all sunlight below $\lambda\lambda$ 2900-3000 is totally absorbed by a very thin layer of ozone at high altitudes of the atmosphere (about 3 mm. if reduced to 760 Hg) is important not only to biologists, but to meteorologists, and astrophysicists, who find it rather disgusting that such a thin film should cause so much trouble in their efforts to get to shorter wave-lengths. It is also interesting from the photochemical point of view. Excluding electric discharges in the upper atmosphere, of which we know practically nothing, we must conclude as a basis for a theory that this ozone layer is caused by a photochemical reaction. Assuming this I have shown in a paper to be published soon,[1] that the photochemical decomposition of ozone by ultraviolet light below $\lambda 2655$ is a primary reaction whilst the formation of ozone requires excited oxygen molecules, the efficiency of which can easily be raised by resonance effects just as I have put forward in the introductory paper. Thus the *two* primary photochemical reactions leading to an equilibrium of O_3 are

$$O_3 + h\nu \quad (<\lambda 2655) = O_2' + O' \quad . \quad . \quad . \quad (I)$$

$$O_2 + O_2'' (<\lambda 2025) = O_3 + O' \quad . \quad . \quad . \quad (II)$$
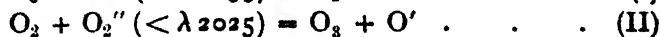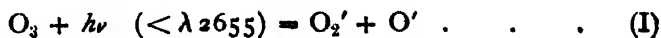
excited atoms being the end products in each case.

[1] R. Mecke, *Z. physik. Chem.*, **B**, 1931.

Assuming now several secondary reactions, varying as excited or ordinary atoms react, I was able to prove that (independently of the assumed secondary reactions), at very low pressure and small ozone concentration (conditions which are undoubtedly met with at high altitudes of the atmosphere), the law of equilibrium concentration is obeyed ($3O_2 \rightleftarrows 2O_3$) :

$$[O_3]^2/[O_2]^3 = K \quad . \qquad . \qquad . \qquad . \quad (1)$$

The constant of equilibrium K contains, first, the different factors of reaction velocities. In one of these factors a three-body collision is involved so that K will be proportional to the total pressure p. It next contains the ratio ϵ_2/ϵ_3 of the mean absorption coefficient for the spectral region which leads to formation of ozone to the mean coefficient of that region which decomposes ozone. Finally K contains the ratio of light intensities I_2/I_3 causing this formation and decomposition. These intensities, of course, will depend on the length of the light path in the atmosphere and may be expressed by

$$I_2 = I_0 e^{-\int_h^\infty \epsilon_3[O_3]dh}, \quad I_3 = I_0 e^{-\int_h^\infty \epsilon_2[O_3]dh} \qquad . \qquad . \quad (2)$$

We may now write equation (1) so that the reaction intensity of ozone formation stands on the right side, whilst on the left side we have the reaction intensity of decomposition

$$[O_3]^2 e^{-\int_h^\infty \epsilon_3[O_3]dh} = C[O_2]^3 p e^{-\int_h^\infty \epsilon_2[O_2]dh} \qquad . \qquad . \quad (3)$$

The formula looks rather complicated but really it is not. To show this we will differentiate the equation (3), assuming that the O_2 concentration will obey the barometric formula, and may, as a first approximation, be set proportional to the atmospheric pressure.[2] We shall get ($H =$ height of the homogeneous atmosphere $= 7{\cdot}99$ km.) :

$$\frac{1}{[O_3]} \cdot \frac{d[O_3]}{dh} = -\frac{2}{H} + \frac{1}{2}\epsilon_2[O_2]\left(1 - \frac{\epsilon_3[O_3]}{\epsilon_2[O_2]}\right). \qquad . \qquad . \quad (4)$$

Now $[O_3/O_2]$ is of an order not exceeding 10^{-3}, so we can neglect $\left(1 - \frac{\epsilon_3 O_3}{\epsilon_2 O_2}\right)$, or take it as fairly constant so long as the mean light absorption in ozone is not greater than 1000 times that of oxygen. I think we may safely assume that.

Integrating formula (4) again, we find the following more simple expression in which p_m denotes the atmospheric pressure of that height which contains the maximum $[O_3]_m$ of ozone concentration,

$$[O_3] = [O_3]_m\left[\left(\frac{p}{p_m}\right)e^{1-\frac{p}{p_m}}\right]^2. \qquad . \qquad . \qquad . \quad (5)$$

It is not difficult to calculate these constants p_m and $[O_3]_m$ from experimental data. Absorption measurements have shown that the mean altitude of the ozone layer[3] is about 50 km. This height corresponds to a pressure of about 10^{-3} atm. Fabry and Bouisson[4] have found that the total thick-

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[2] It is very easy to account for the change of O_2 concentration high up in the atmosphere. The result will be practically the same putting in (4) and (5) instead of $2{\cdot}0$ the factor $2{\cdot}157$, and $(p/p_m)^{1{\cdot}20}$ instead of (p/p_m) in the exponent of e. As the experimental data are not so very accurate it is not worth while taking this change into account.

[3] J. C. McLennan, R. Ruedy, V. Krotkov, *Trans. Roy. Soc., Canada*, **22**, 293, 1928 ; J. Cabannes, J. Dufay, *J. Physique*, **8**, 125, 1927.

[4] Ch. Fabry, H. Buisson, *J. Physique*, **3**, 163, 1913.

ness of the layer reduced to normal pressure is about 3 mm., *i.e.*, 0.4×10^{-6} taking the height of the homogeneous atmosphere as an unit (7·99 km.). Now,[5] integrating formula (5), we get the expression

$$[O_3]_{total} = 1.85\ [O_3]_m \cdot p_m.$$

The maximum concentration being thus $\sim 2.10^{-4}$ c.cm./c.cm. air. This maximum is extremely sharp (see Fig. 1). Raising the pressure to $3.36 p_m$ (~ 3 mm. Hg) will reduce the ozone concentration to one-tenth its maximum and $1/1000[O_3]_m$ is reached at about 6 times the pressure p_m (~ 5 mm. Hg) the concentration diminishing now very rapidly so that at the lowest pressure ever reached in the atmosphere by pilot balloons (30 mm.) no ozone will be found at all. We thus readily understand why no appreciable amount of ozone could be detected experimentally in the atmosphere and whilst at the same time its existence in the upper atmosphere cannot be denied.
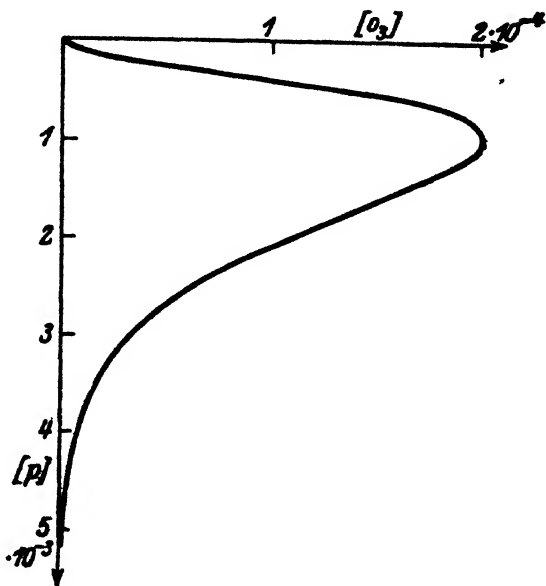
Fig. 1.

In conclusion I will recall the facts on which this statement is based. They are :—

(1) The cause (light) which produces ozone must be reduced while passing the atmosphere according to a simple exponential formula $e^{-\alpha \cdot p}$.

(2) The ozone concentration must be proportional to some power of the atmospheric pressure (O_2 concentration) exceeding one, probably being 2.

(3) The mean absorption of light for that spectral region which causes ozone decomposition must be less than 1000 than strong than that which causes ozone formation.

Considering the primary reactions and all possible secondary reactions involved in this photochemical equilibrium, it is easy to prove that in a very good approximation these statements will hold true.

Heidelberg, Physikalisch-chemisches Institut der Universität.

[5] It is universally $\int_0^\infty (xe^{1-x})^n dx = (n-1)!\left(\dfrac{e}{n}\right)^n \approx \sqrt{\dfrac{2\pi}{n}}$ (Stirling formula), the values are 2·72 ($n = 1$); 1·85 ($n = 2$); 1·49 ($n = 3$); 1·28 ($n = 4$). The exponent n thus does not much affect the result.

ULTRAVIOLET ABSORPTION SPECTRA OF ACETYLENE AND FORMALDEHYDE.

BY G. HERZBERG (*Darmstadt*).

Photochemical reactions are produced only by radiations which bring the molecules into states of an electron configuration other than that of the ground state. Radiations which only excite rotations or vibrations of the molecule (infra-red or red absorption spectra) in general cannot lead to photochemical decomposition. If the potential curve of the upper electronic state involved is one of repulsion [1] a continuous absorption spectrum occurs which corresponds to immediate dissociation of the molecule into its constituents having more or less kinetic and excitation energy. If the upper electronic state has a minimum of potential energy somewhere near that of the ground state the molecule may either not decompose but go back to the ground state with emission of radiation, or decompose by collision or by radiationless transfer without collision (predissociation).[2]

In this way the *photochemical dissociation processes* of *diatomic* molecules have, to a great extent, been explained. As to *polyatomic* molecules, however, very little has been done so far. The continuous and diffuse absorption spectra exhibited by these molecules in the gaseous state [3] in addition to discrete absorption bands, evidently correspond also to photochemical dissociation : a detailed explanation has not yet, however, been given in most cases.

In order to obtain a better knowledge of the photochemical dissociation processes in polyatomic molecules it is necessary, in the first place, to get better information as to the electronic levels of polyatomic molecules ; that is to say one has to investigate the *electronic band spectra* (ultraviolet absorption spectra) of these molecules. Until now none of these spectra has been completely explained. The electronic band spectra of some of the simplest polyatomic molecules even are completely unknown because they lie in the far ultraviolet.

With this in view G. Scheibe and the author [4] have recently investigated the far ultraviolet absorption spectra of the *methyl halides*. The discrete absorption bands they found in the far ultraviolet correspond to transitions into stable electronic states of these molecules lying very high above the ground level.[5] There was, however, a region of continuous absorption lying

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[1] At least for nuclear distances of the same order of magnitude as that of the potential minimum of the ground state.

[2] Pre-dissociation and related phenomena will be discussed in a forthcoming review of the author in the *Ergebn. exakten Naturw.*

[3] In the liquid or solid state continuous bands occur very often, but must not correspond to photochemical dissociation.

[4] G. Herzberg and G. Scheibe, *Trans. Farad. Soc.*, **25**, 716, 1929, and *Z. physik. Chem.*, B **7**, 390, 1930.

[5] The frequency of vibration in two of the upper states of CH_3I is 1090 cm. $^{-1}$ and 1030 cm. $^{-1}$ respectively, corresponding to a transverse vibration of the H-atoms in the CH_3 group. So far no other frequency of the excited state could be analysed. Exposures taken at higher pressures revealed two frequencies of the ground-state, namely, 1250 and 520 cm. $^{-1}$. The first also found by Bennet and Meyer (*Physical Rev.*, **32**, 888, 1928) in the infra-red presumably is a transverse vibration of the H-atoms in the ground state, corresponding to that of the excited state. The latter frequency was also observed by Dadieu and Kohlrausch (*Wien. Ber.*, **139**, 77, 1930) and is a valency vibration $CH_3 \rightleftharpoons I$ *cf.* below).

at *longer* wavelengths than the discrete bands. It was shown that this continuous absorption corresponds to the *photochemical dissociation of the halide* into normal CH_3 and slightly excited halogen (^2P) or into slightly excited CH_3 and normal halogen (^2P) with various amounts of kinetic energy. The maximum of continuous absorption corresponds to dissociation with very high kinetic energy (about 2 volts = 46 kal./mol. in the case of CH_3I). The upper electronic state involved is one of nearly pure repulsion.[6]

For the same reasons as given above the author has taken absorption spectrograms of two other simple polyatomic molecules, namely *acetylene* (C_2H_2) and *formaldehyde* (H_2CO). Acetylene has also been chosen for investigation because of the very simple fine structure found by Mecke and co-workers [6a] in the infrared. Mecke has already pointed to the close similarity to be expected between C_2H_2 and N_2 because both have the same number of electrons. Such a similarity is also to be expected between H_2CO and O_2, especially with regard to the electronic levels.[7] There are of course other polyatomic molecules which resemble certain diatomic molecules in the same manner as above. It is hoped to investigate some of these later.

The experimental procedure was quite the same as that in the previous paper [4] except that a two meter vacuum spectrograph was used.[8]

Acetylene.

C_2H_2 has no absorption until λ 2070 at pressures up to 30 mm. and 20 cm. length of the absorption tube. Here a system A of very weak absorption bands extends to shorter wavelengths with increasing intensity.[8a] The regularities are not obvious. The distance of the main bands is 1365 and 865 cm. $^{-1}$. Another very strong system B of absorption bands begins at about λ 1540—depending on the pressure. Unfortunately, in this region the continuous spectrum of hydrogen which served as background has already faded away, and there is only the many line spectrum of hydrogen. Nevertheless, the discrete structure of this strong absorption is quite clearly to be seen on the plates. The distance of the main bands is about 1710 cm. $^{-1}$. The structure of these bands will further be investigated with a Lyman source of continuous radiation as background.

It seems to the author that the strong system B corresponds to the Lyman-Birge-Hoppfield bands, the first ultra-violet absorption system of N_2 beginning at about 1450 A.U. The shift to longer wavelengths is what

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[6] *Cf.* Fig. 11 of the above-mentioned paper.

[6a] K. Hedfeld and R. Mecke, *Z. Physik*, **64**, 151, 1930, W. H. J. Childs and R. Mecke, *ibid.*, 162, 1930, R. Mecke, *ibid.*, 173, 1930.

[7] It is well known that all diatomic hydrides show a pronounced similarity to the united atom.

[8] This vacuum spectrograph was designed by Dr. Skinner and built in the workshop of the H. H. Wills Physics Laboratory (Bristol) where the work was carried out.

[8a] Shortly after this paper had been sent away a paper by Kistiakowsky (*Physical Rev.*, **37**, 276, 1931) appeared on the ultraviolet absorption spectrum of acetylene. Kistiakowsky used absorption tubes of 2 m. length and atmospheric pressure of C_2H_2. So he got absorption bands at λ2400. There seems little doubt to me that his bands are the continuation of those discussed here to longer wavelength. I found that on increasing the pressure from 1 to 30 mm. the long wavelength limit shifted considerably to longer wavelength, so that it is quite possible that at atmospheric pressure and 2 m. length of absorption tubing the limit is at λ2400.

one might expect in going from a diatomic to a polyatomic molecule. The weak system A is believed to correspond to the transition from the normal $^1\Sigma$ to the first excited $^3\Sigma$ level of N_2, a transition which is absolutely forbidden in N_2 but which might occur weakly in C_2H_2. The distance of the main bands in both systems A and B is not in contradiction to this analogy. Anyhow the existence of two different stable electronic levels in C_2H_2 is proved by the observation of the two band systems A and B. As to the energies of dissociation and products of dissociation in these states nothing definite can be said until now because the vibrational analysis of the bands is rather difficult in consequence of the existence of several vibrations and is not yet finished.

At higher pressures a continuous absorption sets in at about λ 1880. It is not absolutely certain whether this is really due to C_2H_2 and not to an impurity. In the first case it might correspond to a dissociation of C_2H_2 into two normal CH-radicals. But this would lead to a pretty low value for the binding energy of the C—C bond. The possibility that it corresponds to a photochemical dissociation into HC—C and H seems rather more likely.

Formaldehyde.

The absorption spectrum of H_2CO in the near ultra-violet has already been investigated by V. Henri and S. A. Schou.[9] They have found

FIG. I.
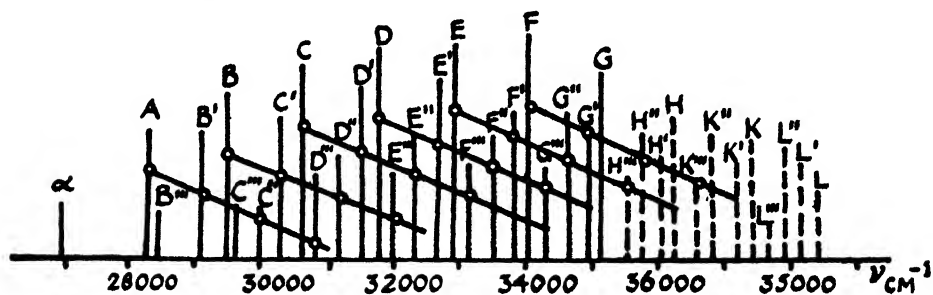
a system of discrete absorption bands beginning at about λ 3570 with clearly resolved fine structure due to the small moment of enertia round the C$=$O axis. At a certain point the fine structure of these bands disappears, the bands become diffuse (predissociation) and then gradually mix into a continuous absorption. On the author's plates the discrete and diffuse bands are also present, whereas the continuous absorption is absent or very weak. A good spectrogram of these bands has already been published by Henri and Schou. . The distance of the main bands, which they call A, B, C . . . is 1187 cm.$^{-1}$ and is gradually decreasing. Each of these is accompanied by a somewhat weaker band B', C', . . . on its long wavelength side (cf. Fig. 1 for a diagrammatic representation of the bands) except that the A band has no such companion. This fact is very important for a correct interpretation of the vibrational structure of this band system, but has not been regarded by Henri and Schou. They, therefore, interpreted the main and satellite bands in the manner shown in Fig. 2. The larger vibrations of the upper level are numbered by the quantum number v' the smaller ones by w'. For every vibrational level

[9] V. Henri and S. A. Schou, Z. Physik, **49**, 774, 1928.

v' the values $w' = 0, 1, 2, \ldots$ are possible. According to Henri and Schou the main bands A, B, . . . correspond to transitions from the vibrationless [10] level of the ground state ($v'' = 0$, $w'' = 0$) to the levels $v' = 0, 1, 2, \ldots$ with $w' = 1$ of the upper electronic state, the satellite bands correspond to similar transitions only with $w' = 0$, so that the distance $B'B$ (361 cm. $^{-1}$), $C'C$, . . . is the second vibration in the upper level. The transition $v'' = 0$, $w'' = 0 \to v' = 0$, $w' = 0$ is not observed according to this interpretation. No plausible reason can be given for this. Therefore, we give another interpretation in Fig. 3 (also indicated in Fig. 1) which immediately explains why the first main band has no satellite. Correctly speaking, according to this new interpretation B' is the satellite of A, C' that of B, etc., so that the main bands A, B, . . . correspond to transitions to different v' levels with $w' = 0$ whereas B', C', . . . have $w' = 1$ ($v' = 0, 1, \ldots$). Bands with $w' = 2, 3, \ldots$ are also present, though the intensity decreases rapidly in a w' progression. Whereas
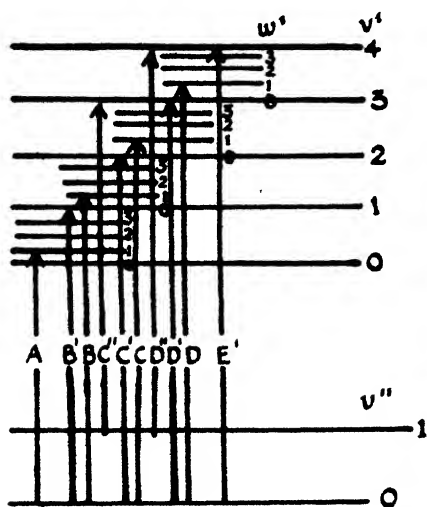
FIG. 2.
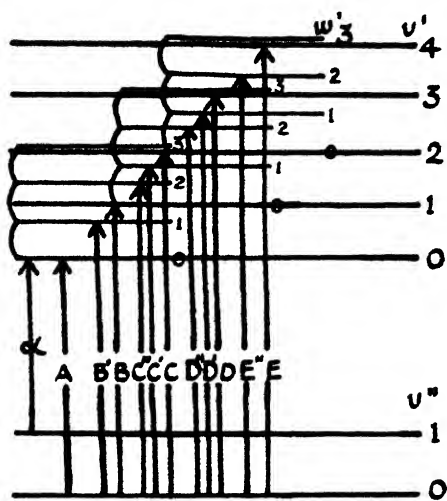
FIG. 3.

according to the new interpretation the larger vibrational frequency is rather the same as according to Henri and Schou namely 1187 cm. $^{-1}$ the smaller one is now 830 cm. $^{-1}$ (distance AB', BC', . . .) against 360 cm. $^{-1}$ of Henri and Schou.

The superiority of the new interpretation is further shown by the fact that it is no longer necessary to assume that certain bands correspond to transitions from the higher vibrational states of the ground state to the upper state, as was done by Henri not only in this case (*e.g.* bands C'', D'' . . .) but also in many other cases. According to the Boltzmann factor such bands ought to be extremely weak compared with those corresponding to the vibrationless state, a condition not at all fulfilled in Henri's analysis.

A band which however certainly is a transition from the first vibrational level of the ground state is the very weak one called a by Henri and Schou (see Fig. 1). It lies on the long wave-length side of band A. The distance

[10] We neglect the half-quantum zero-point vibrational energy of the quantum mechanics because it does not alter the conclusions.

1300 cm.$^{-1}$ should be a vibrational frequency of the ground state[10a]. A similar interpretation applies to the very weak bands B''', and C'''.

A rigorous test of this new analysis cannot be made unless the fine structure of the bands is analysed, because they are very wide and without pronounced heads. In fact Henri and Schou have analysed the fine structure, but there are several inconsistencies in their analysis, e.g. the values

$$B'' = \frac{h}{8\pi^2 c I''} \quad (I'' = \text{moment of inertia of the lower state}) \text{ for the } A, B, C,$$

. . . bands decrease just in the same manner as the B' values, though all these bands even according to Henri and Schou have the same lower level.[11] Therefore it is proposed to reinvestigate the fine structure. Besides an exact constancy of the first quantum of vibration w' for different values of v' cannot be required because the superposition of two frequencies is not exactly the sum of both (cf. also below). The differences AB', BC', . . . as calculated from Henri's data in fact increase.

If we follow the analogy between H_2CO and O_2 it seems probable that the Henri-Schou bands correspond to the Schumann-Runge bands of oxygen. The shift to longer wavelengths is again in agreement with what one might expect for a polyatomic molecule.

Raman effect and infra-red investigations have revealed the existence of two types of vibrations in polyatomic molecules[12] *valency vibrations* and *transverse vibrations*, i.e., vibrations in the direction of a chemical bond and perpendicular to it (stretching and bending of the bond). The larger frequency 1187 cm.$^{-1}$ observed in the excited state of H_2CO is presumably the valency vibration of $CH_2 \longleftrightarrow O$, i.e., it is analogous to the vibration $O \longleftrightarrow O$ of oxygen in the upper $^3\Sigma$ state of the Schumann-Runge bands, whereas the smaller frequency 830 cm^{-1} of H_2CO is probably the transverse vibration of the H-atoms ($H \longleftrightarrow H$). Both observed vibrations cannot be $C \longleftrightarrow H$ vibrations because this always has been found to be about 3000 cm.$^{-1}$, a value which cannot be altered very much for the excited state, because the excitation lies in the $C = O$ bond. The transverse vibration of the H-atoms, which for the normal state usually is found to be about 1300-1500 cm.$^{-1}$ may well be lowered by the excitation in the $C = O$ bond because the corresponding potential curve is determined by the position of the O nucleus. A transverse vibration of the O nucleus presumably would give a much smaller frequency than those observed.

The fact that the larger vibration decreases in the same manner as in a diatomic molecule, whereas the smaller one remains constant or even increases with increasing vibrational quantum number is further support for our interpretation of the two vibrations. Diatomic molecules have only one valency vibration which decreases with increasing quantum number. The potential curve for transverse vibrations is composed of two repulsion curves (repulsion from the two neighbouring atoms), i.e., it may be on both sides steeper than a parabola and so the frequency of vibration may well increase with increasing quantum number, as it does according to Henri and Schou's data.

The rapid decrease of intensity in a w' group ($v' = $ const.) and the slow increase and decrease of intensity in a v' group is easily explained by Franck's principle, if one considers the potential curves of Fig. 4 and

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[10a] Similar bands have been found in the case of CH_3I (cf. notes 4 and 5).

[11] *Cf.* also the infra-red investigations of E. O. Salant and W. West (*Physical Rev.*, **33**, 640, 1929).

[12] *Cf. e.g.* D. H. Andrews, *Physical Rev.*, **36**, 544, 1930, and R. Mecke, *Z. Physik*, **64**, 173, 1930.

remembers that the potential curves are the narrower the larger the quantum of vibration.

As in O_2 the dissociation [13] by increasing the vibrational energy in the upper state of the Henri-Schou bands presumably leads to normal O and excited CH_2 or excited $O(^1D)$ and normal CH_2, the excitation being of the order of a few volts.[14] The total amount of energy for this dissociation from the ground state is found by extrapolation to be 69,000 cm.$^{-1}$ or 195 k.cal./mol. From chemical heats of combustion one gets a value 155 k.cal./mol. for the dissociation into normal O and normal CH_2, so that the energy of excitation is of the right order corresponding presumably to O^1D.

The beginning of predissociation (λ 2750)[15] corresponds to the overlapping of another electronic level which is continuous in that region (a' of Fig. 4). As pointed out by the author[16] the beginning of predissociation only gives an upper limit to the dissociation energy of the normal molecule. This limit is 105 k.cal./mol. It therefore cannot correspond to the dissociation $CH_2 + O$ but must be $H_2CO \rightarrow H + HCO$,[17] as was shown by

Mecke some time ago.[17a] The photochemical dissociation of H_2CO in the region of predissociation and even near its limit occurs with rather large amounts of kinetic energy, the energy of the same dissociation ($H_2CO \rightarrow H + HCO$) calculated from chemical data being 92 k.cal./mol.

Even at a somewhat high pressure (50 mm.) no absorption was noted in H_2CO between λ 2500 and λ 1650. At λ1650 a very strong discontinuous absorption begins (at lower pressures at λ 1560). Unfortunately as in C_2H_2 the many line spectrum of hydrogen prevents an accurate measurement of the bands. But three bands are

FIG. 4.

clearly defined, the distance of which is 1180 cm.$^{-1}$.[18] These bands are the transition of the molecule to a new stable electronic level of high energy. But though it is stable if left by itself, it will not be stable against collisions with other molecules and, therefore, will be active photochemically, the different energies of dissociation of the normal molecule being much smaller than its energy content. The same considerations, of course, apply to the upper state of the B bands of C_2H_2.

Hitherto no state of O_2 analogous to the above-mentioned state of H_2CO has been found. It should lie still further in the ultra-violet. It might be,
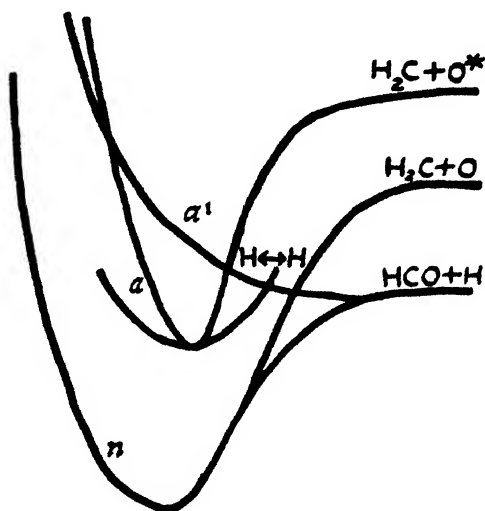
[13] G. Herzberg, Z. Physik. Chem., B 4, 223, 1929.
[14] In the case of oxygen the excitation is 1·96 volt, cf. 16.
[15] The limit is not sharp.
[16] G. Herzberg, Z. physik. Chem., B 10, 189, 1930; Z. Physik, 61, 604, 1930.
[17] The reason that no such predissociation can occur in the case of oxygen is obvious.
[17a] R. Mecke, Nature, 125, 526, 1930.
[18] The structure of these bands also will further be investigated with a Lyman continuous spectrum as background.

however, in this case (and in that of C_2H_2 as well) that the far ultraviolet bands correspond to an electron jump of the C—H bond.

I hope to discuss this matter further and in more detail when the analysis of the bands discussed above has been completed.

Summary.

The ultraviolet absorption spectra of C_2H_2 and H_2CO are investigated with a 2 m. vacuum spectrograph. Both of these molecules show two regions of discontinuous absorption corresponding to two stable excited electronic levels of these molecules. The longer wavelength system of H_2CO has already been discovered by Henry and Schou. Their vibrational analysis is corrected here. The vibrations and photochemical processes in the different states of these molecules are discussed.

GENERAL DISCUSSION.

On Part I., Papers 1, 1a and 2.

Professor R. Mecke (*Heidelberg*) said : Dr. Herzberg desires me to say that he regrets very much not being able to be present to-day. But since I had the opportunity of discussing the subject with him at Heidelberg only a few days before leaving for England, I will read his paper, and I will make some additional remarks as to what in the near future the programme in analysing electronic band spectra of polyatomic molecules will be, and how some photochemical conclusions can be drawn from the results to be expected. First, I must once again emphasise, that up to now there is no single case where spectroscopicists have succeeded in analysing an electronic band system of any polyatomic molecule to any degree of certainty, although I am quite hopeful that this will be the case in the near future. To show here the outline in the analysis which has to be followed up, I will call attention to Table I. This contains simple molecules, di- and polyatomic,

TABLE I.

X≡X.		X=X.		X—X.	
N≡N	(2345)	O=O	(1565)	F—F	(1132)
C≡O	(2150)	(H_2C)=O	(1768)	(H_3C)—F	(1048)
HC≡N	(2090)	(H_2C)=(CH_2)	(1623)	(H_3C)—(CH_3)	(990)
HC≡CH	(1975)			(H_2N)—(NH_2)	(908)
				(HO)—(OH)	(860)

with the same number of electrons : 14, 16, and 18 respectively. It is expected from well-known laws that their spectra will behave in similar ways. The numbers in parenthesis are the observed valence vibrations characteristic for the threefold, double, and single linkage in the valency bond. Taking the first column we now know from infra-red investigations all the molecular data for the ground level : the nuclear distances and the different valence and deformation oscillations (5 in the case of C_2H_2, 3 in the case of HCN). We know, too, several excited electronic levels of the two diatomic molecules N_2 and CO. Of special interest here are the two levels next to the ground level causing light absorption in the ultraviolet ; one of these two levels is always metastable. But in every case the excited levels correspond to only double bound molecules, one linkage of the bond being split up by electronic excitation. This is clearly shown by the sudden drop of the valence vibration from about 2100 down to about 1600 (N_2 : 1680 and 1718 ; CO : 1500 and 1725).

Thus these molecules excited by light absorption will behave chemically in the same way as ordinary (unexcited) oxygen.

Now Dr. Herzberg has found that there are the same two excited states in the case of acetylene, and that there is the same drop in the valence frequencies. Since the absorption measurements of Landau and Henri have turned out to be due to impurities, the investigations of Dr. Herzfeld and Kistiakowsky ought to be carried on ; moreover, similar work ought to be done upon the hydrogen cyanide molecule, where no results are known to me. I have no doubt that these investigations will be successful, and then the first column will be completed. Turning to the second, we now know—in addition to the data for the ground level—two excited levels of oxygen, one metastable, causing very weak absorption in the red, and one producing the strong ultraviolet absorption of oxygen. In the metastable state the bond remains this time the same (double linkage : 1420), but by ultraviolet absorption the oxygen molecule is changed into a single bonded compound ($\dot{O}$—$\dot{O}$), the sudden drop of the valence oscillation (708) is apparent. Coming now to the second molecule of this column I agree with Dr. Herzfeld that the analysis of Henri and Schou must be wrong to a great extent, since essential rules of a spectroscopic analysis are not obeyed (e.g. the combination principles). The analysis of Dr. Herzberg is very much more consistent in this respect. But, of course, it is not easy to give a complete analysis right away. It has to be remembered that in each state six different vibrational frequencies exist, which must be established by the analysis. Five frequencies of the ground level—found by Raman investigation—seem to me to be 920, 1040, 1460, 1770, and 2945. The sixth missing one has also the value 3000. In the list of polyatomic molecules which ought to be investigated at an early date, I would include ethylene (C_2H_4). The double bonded C=C linkage is (as a so-called "chromophore ") of great importance in organic chemistry. In this way the photochemical and the spectroscopic analysis of ethylene will certainly reveal the understanding of many chemical reactions of unsaturated hydrocarbons.

I must omit the third column since only few reliable data are available now. At any rate, the results gained in the analysis of diatomic molecules will always be a good guide in the investigation of polyatomic molecules. I am certain that the knowledge (photochemical as well as spectroscopic) we gain here will increase rapidly in the next few years.

Professor M. Bodenstein (*Berlin*) said : (1) In amplification what Professor Mecke says in connection with his Table II., I can state that Jost [1]

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[1] Jost, *Z. physik. Chem.*, **134**, 92, 1928.

has made experiments on the behaviour of bromine illuminated with that part of its band spectrum which contains energy sufficient to produce dissociation into two normal molecules. In this case the excited molecules can be broken into atoms when a collision occurs. In gases at atmospheric pressure these collisions occur during the life-time of the excited state and, indeed, bromine reacts towards hydrogen just as in the continuous region.

An opposite result has been found by Schumacher and Stieger in a research just published.[2] In CCl_4 solution the yield of the decomposition of C_2H_3I in the band-region—of a sufficient energy, of course—is about six times smaller than in the continuous absorption.

A third investigation of this kind has been made in my laboratory within recent months by Hertel. The reaction between illuminated chlorine and hydrogen molecules, if excited molecules are produced in the band spectrum, follows a law different from that which applies when the atoms are produced by shorter wavelengths.

(2) I was extremely interested in the suggestion that the spectrum of acetylene indicates a splitting up of one valence by the ultra-violet absorption

$$HC \equiv CH + E = H\overset{.}{C} = \overset{.}{C}H.$$

In discussing a paper of Spence and Kistiakowsky[3] dealing with the kinetics of the thermal oxidation of acetylene, I have just made[4] the same assumption for the primary step of this reaction. This step is followed by an addition of oxygen just as mentioned by Mecke with the difference only that the " moloxyde " thus formed does not give rise in every case to the formation of glyoxal but sometimes changes into other products.

There is, however, an important difference between the photochemical and the thermal production of this excited acetylene molecule. Ultra-violet light has an energy of more than 100 Cal. per Einstein whilst the activating energy of the thermal reaction is only $34 \cdot 7$ Cal. per mol. One must conclude, therefore, that both these excited states are not the same. Robinson, at the recent meeting of the Institut International de Chimie Solvay in Brussels, suggested an interpretation for the slight excitation by using the language of the electronic theory of the valence. This is given by the symbols $H : C \mid C : H$ normal state, all electrons shared, and $H : C \mid C : H$ or $H : C \mid C : H$ excited state, one of the six CC electrons unshared thus producing a polarisation.

I will not discuss the question whether this interpretation is correct ; I only want to state that here in the case of acetylene photochemical excitation is not of the same nature as thermal excitation and that a similar difference may also occur in other cases.

Professor Mecke said : I am very glad to hear from Professor Bodenstein that, in addition to the work of Norrish on the NO_2 decomposition, at least in three other cases a difference in behaviour of a photochemical reaction could be shown experimentally below and beyond the convergence limit or the threshold of sensitised dissociation, thus proving that my Fig. 3, which was drawn merely from spectroscopic reasoning, is qualitatively correct. Up to now very little work has been done with monochromatic light in the neighbourhood of a photochemical threshold, but I think that photochemical investigations ought to be pushed forward especially in

[2] Schumacher und Stieger, *Z. physik. Chem.*, **B 12**, 378, 1931.
[3] Spence and Kistiakowsky, *J. Amer. Chem. Soc.*, **52**, 4837, 1930.
[4] *Z. physik. Chem.*, **B 12**, 151, 1931.

this direction in order to settle beyond doubt the different questions connected with the primary process of a photochemical reaction.

Coming to the second point raised by Professor Bodenstein I absolutely agree with him that there is quite a difference between the photochemical and the thermal oxidation of acetylene. But in the case of the absorption of ultraviolet light by acetylene we perfectly well know that every reaction which will take place on account of this absorption has to deal with a molecule H—$\dot{C}$=$\dot{C}$—H in which one valency has been split up. With regard to the thermal reaction we know little; but I should think that some such polarising effect will take place as Professor Bodenstein and Robinson suggested at the meeting in Brussels. As Professor Bodenstein has pointed out, we already know many reactions (I mention only CO, CH_4, etc.) in which the thermal heat of activation is very much smaller than the first excited state known to us spectroscopically, so that this behaviour is general rather than exceptional. It is always, however, the very great advantage of a photochemical reaction that in this case we are able to apply " highly concentrated energy by means of light quanta to single molecules " and that at the same time by the spectra produced we can " see " what happens. We can never do this in the case of thermal reactions, but we have to take a similar photochemical reaction as a guide.

Professor J. Eggert (*Leipzig*) said : Professor Mecke in his paper has quoted our experiments on silver bromide as an example of a primary reaction with quantum yield 1. According to his view it follows that the effect of the sensitiser must be conceived simply as effecting a shift of the absorption band of the silver bromide (about 4600 Å. and less) towards higher wavelengths ; at the same time Professor Mecke considers it more likely that by reason of the adsorption of the dyestuff at the crystal surface the amount of energy necessary to bring about dissociation is so far reduced that the decomposition can thus be brought by quanta of lower energy. On this point I would say : (1) It is well-known that decomposition of silver bromide in the green or red is possible in the absence of a sensitising dyestuff. We know, for example, that the red light of the dark-room lamp (about 6500 to 7000 Å.) has an effect on the photographic plate on long exposure, and in this it seems to me there is a difference between this system and the conditions with gases. (2) The increase in the sensitivity of photographic plates for radiation of long wavelength under the influence of sensitisers can further be explained on the assumption that a dyestuff-silver compound is formed of which the absorption bands at long wavelengths correspond to a substantially lower dissociation energy. On the other hand, the following observations made first by Leszynski and later confirmed by Tollert contradict this ; if we compare for *strong* illumination (and without subsequent development) the number of silver atoms produced and the number of corresponding dyestuff molecules we find that *one* adsorbed sensitising molecule (erythrosin) is capable of leading to the production of as many as 80 silver atoms. This circumstance appears to me to be inconsistent with the assumption that a dyestuff-silver compound is decomposed under the influence of light of long wavelength, because the compound must always be reformed. It appears to me that a much simpler explanation is that the dyestuff itself (as suggested by Franck) takes up the energy, transfers it to the Br^- ion of the AgBr lattice and frees from the latter an electron with formation of a bromine atom ; the electron would finally discharge a silver ion as in the normal process. The fact that the same dyestuff molecule undergoes this process many times indicates that it is freely mobile, as we know it is the case in other examples.

This conception of the sensitisation phenomenon moreover depends upon purely photographic considerations.

Professor Mecke in reply said : I think that the very small sensitivity of silver bromide in the red and green is due to some sensitising process, caused also, maybe, by the *Farbzentren* which in a recent paper Hilsch and Pohl have shown to absorb in this region thus producing secondary photochemical reactions.

I, also, do not think that in the sensitising process a new silver dyestuff compound in the ordinary sense is formed, but I think that straightforward adsorption takes place, which changes the absorption spectrum by means of disturbances in the crystal lattice. Now the distance of the Ag and Br atoms in this lattice is $2 \cdot 89 \times 10^{-8}$ cm. and surely such a complicated thing as a dyestuff molecule is very much bigger than that. For this reason it is easy to imagine that this molecule will cover or at least affect eighty or more AgBr molecules. Of course, in any case, the dyestuff will absorb the energy and will transfer it to the AgBr molecule, but the energy to dissociate these molecules is lowered by the adsorption. With these remarks it is not my intention to put forward a well-founded theory of the sensitising process (it is hard to do that in the case of a photographic plate) but rather to make some suggestions—which may prove to be entirely wrong—in order to provide a starting-point for a theory where now there is none.

Mr. C. F. Goodeve (*London*) said : Professor Mecke places an interpretation on the absorption spectrum of water vapour which differs from that which we give in a paper later this morning. No decision as to the correct interpretation can be made until the type of absorption shown by water vapour has been definitely established. I believe that the fine structure shown on Leifson's photographs is due to strong hydrogen emission lines, and Leifson himself considers that water vapour shows only continuous absorption. Further examination with higher dispersion instruments may resolve the absorption band into fine structure, but this is not to be expected unless the continuous absorption of other ionic compounds such as H_2S, HBr, etc., is also resolvable. Furthermore, molecules exhibiting band systems show generally a gradual increase in extinction coefficient with increasing frequency and not a sharp threshold as found for water and other compounds of this class. So far as present evidence shows the primary process of light absorption is dissociation of the water molecule.

A second point I would like to discuss concerns the heat of dissociation of oxygen. The "accepted value" for this heat has varied over wide limits within the last few years. As is well known the convergence of the oxygen bands is at 1753 Å., corresponding to 162 Cal. The products of dissociation at this wavelength are believed to be a normal and a ^1D metastable oxygen atom. The heat of dissociation of oxygen into normal atoms can be determined if the energy difference between the normal and the ^1D level is known. Several attempts have been made to find an approximate value for this level, but no definite success was made until Frerichs [5] analysed the complete OI spectrum and found that this level corresponded to 1·95 volts or 45 Cals. The heat of dissociation of oxygen into normal molecules becomes 117 Cals. This is apparently the source of the value used by Professor Mecke.

Direct calorimetric methods, as employed by Copeland,[6] and by Rodebush and Troxel,[7] give consistent values in the neighbourhood of

[5] *Physical Rev.*, **36**, 398, 1930.   [6] *Ibid.*, **36**, 1221, 1930.
[7] *J. Amer. Chem. Soc.*, **52**, 3467, 1930.

131 Cals., but it is difficult to estimate the absolute limits of error of their measurements. Of the large number of methods based on photochemical behaviour and indirect spectroscopic determinations, little need be said as these methods involve unproven assumptions or have high limits of error. A complete list of references to these methods is given in the above mentioned papers.

An exact and dependable value for the heat of dissociation of oxygen would be of immense value to the advance of photochemistry, and I would like to ask Professor Mecke: (a) Is it his opinion that the present analysis of the OI spectrum is final? (b) Can it be definitely concluded that the convergence limit of the O_2 bands corresponds to the heat of dissociation of oxygen plus the energy of the ^1D level, and what are the limits of error? (c) Is he aware of any indirect methods that give reliable values?

Professor Mecke, in reply, said : Mr. Goodeve raises some questions as to the reliability of the new value of the dissociation energy of oxygen : I think that the present analysis of the OI spectrum is final with regard to the excitation energy of the ^1D level (1·957 volts).

I can hardly imagine another explanation of the ultraviolet dissociation of oxygen. It has been proved that at least one atom of the dissociation products must be in an excited state, which from theoretical reasoning must be the ^1D level. In addition to this, the ^1D level is the lowest excited level possible, and any other level would lower the dissociation energy considerably (e.g., the next level, ^1S, would give only 66 cal.). The convergence of the ultraviolet absorption bands of oxygen is very good, the last band actually measured ($\lambda 1756·7$; $v = 18$), lies within a few Angström units of the convergence limit ($\lambda 1750$). Thus we come to the conclusion that the dissociation energy is correct within about half a calorie : 117·5 ± 0·5.

Indirect methods, more or less accurate, and already mentioned in my introductory paper, are calculations (1) from photochemical threshold measurements, e.g., NO_2 decomposition giving a possible range of 117-128 cal., (2) from heats of combustion and from other well-known dissociation energies, e.g., the measured H_2O decomposition (112 cal.), together with the well-founded assumption that the OH radicle is only a little less firmly bound than the H in water, giving a value of about 120 cal.

With regard to other points mentioned by Mr. Goodeve, I would refer to the remarks of Dr. Herzfeld communicated to the discussion.[8]

Professor A. J. Allmand (*London*) (*communicated*), said : I should like to put to Professor Mecke a point arising out of his paper, and also to ask him a further question less directly connected with it.

(1) I understand that the probability of the reaction

$$A(e_1) + B \rightarrow A + B(e_2) + [e_1 - e_2]$$

where $e_1 > e_2$ and round and square brackets denote internal energy and kinetic energy of translation respectively, is greater the smaller $[e_1 - e_2]$. In this case, I presume that the same must hold for the reverse reaction, and also that, the smaller $[e_1 - e_2]$, the more likely is the reaction

$$\underbrace{A + B}_{(e_2)} + [e_1 - e_2] \rightarrow AB(e_1)$$
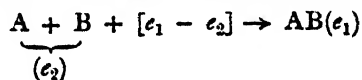
to take place.

If so, the case would correspond to the views of Langmuir[9] and of Lord Rayleigh,[10] on the effect of increased temperature in diminishing

[8] See page 402.   [9] *J. Amer. Chem. Soc.*, 41, 186, 1919.
[10] Strutt, *Proc. Roy. Soc.*, 87, 179, 1912.

respectively the rate of clean-up of nitrogen by a heated molybdenum filament and the intensity of the glow of active nitrogen. Neither of these authors, of course, speaks of a three-fold collision, but Langmuir specifically regards the molecules thus formed as *adsorption complexes*, and is clear that their stability is limited by the difficulty of giving up the liberated energy.

Is a three-fold collision *necessary* for the stabilisation of such *adsorption complexes* so that their life can exceed that of the pseudo-molecules of Born and Franck ? Applied to the specific case mentioned later in the discussion on Part II., is the reaction

$$Cl + H_2O \rightarrow Cl, H_2O$$
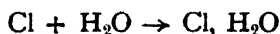
possible without the intervention of a third body ? If so, is it more likely to take place if the kinetic energy of translation of the Cl atom is low ?

(2) The second question concerns the interpretation to be put on the maximum in a continuous absorption band. For example, in the case of the visible band for Cl_2 gas, the maximum lies at about 330-340 $\mu\mu$. Presumably those Cl_2 molecules in the state of greatest probability from the point of view of light absorption, are particularly fitted to absorb the quanta corresponding to this wavelength region, whilst there are comparatively few Cl_2 molecules which can absorb quanta in the region of, say, 280 $\mu\mu$ or 400 $\mu\mu$. What is the likely physical interpretation of these differences in probability states of chlorine molecules which make " collisions " between molecules and quanta more fruitful when the latter are of certain favoured magnitudes? Is there any connection with the state of the chlorine molecule in respect of energy content, *e.g.*, molecules of low energy content tending more readily to absorb large light quanta, and vice versa, and hence some degree of correspondence between such an absorption curve and a Maxwellian energy distribution curve ?

Professor Mecke, in reply, wrote : I should imagine that processes such as those which Professor Allmand mentions under (1) are very likely to exist. I recall the fact that, in ionising gases by electronic rays, the higher the speed of the electrons the smaller is the capacity for ionisation. For electrons of very low velocity we shall get, by some resonance effect, the well-known cross-section curves (Ramsauer, *Wirkungsquerschnitte*). But, of course, it is not easy to detect in the same way processes in chemical reactions between *neutral* atoms or molecules. For these reasons I think it is not impossible that some details of the hydrogen-chlorine reaction may be explained by such processes as he has mentioned.

With regard to Professor Allmand's second question, I would refer to my Fig. 1, case 1, in the introductory paper. This is precisely the case corresponding to the absorption of chlorine. Starting from the not very vigorously vibrating molecule in the ground state, the molecule will, by absorption of light, attain a vibrational energy which it cannot sustain without dissociation.

The arrows drawn in Fig. 1 correspond, according to Condon, in every case to the greatest transition probability. Therefore the absorption maximum in the spectrum depends only upon the situations of the two potential curves relative to each other. In the case of chlorine it is 1400A. beyond the convergence limit within the region of continuous absorption (3400A.) ; with bromine it is only 900A. beyond the convergence limit (5110A.) ; and with iodine the maximum of absorption is superposed precisely on the limit (5000A.).

Dr. R. G. W. Norrish (*Cambridge*) said : In view of the statement about the primary photochemical dissociation of formaldehyde made by Dr. Herzberg in his very instructive paper, I should like to emphasise the point that emerges from the paper to be read by Mr. Kirkbride. It would seem that unsymmetrical carbonyl compounds tend to decompose in their predissociation region *practically exclusively* according to the equation :

$$\begin{array}{c} R_1 \\ \diagdown \\ CO \rightarrow R_1R_2 + CO. \\ \diagup \\ R_2 \end{array}$$
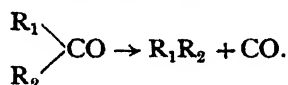
There is no evidence of the production of any R_1R_1 or R_2R_2 nor of the polymerised products of the radicle $-$ RCO. We cannot therefore write an equation involving free radicles such as

$$\begin{array}{c} R_1 \\ \diagdown \\ CO \rightarrow R_1 + R_2CO \\ \diagup \\ R_2 \end{array}$$
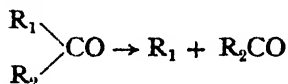
as the primary change, even if R_1 is a H atom, but must admit that the whole decomposition to carbon monoxide and hydrocarbon takes place in one act. It is therefore preferable to write the primary formaldehyde decomposition as

$$\begin{array}{c} H \\ \diagdown \\ CO \rightarrow CO + H_2. \\ \diagup \\ H \end{array}$$
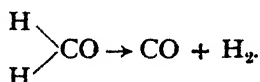
We may say, if we wish, that one radicle is eliminated very quickly after the other, though I do not think that this assists a mental picture of the process very materially. The essential feature is that the free radicles from a given molecule never separate, but react among themselves to form stable products. The cogency of the chemical evidence must be admitted, and though it does not assist greatly to visualising the process of predissociation we must accept the results which indicate clearly the nature of the primary photochemical change. Recent events in atomic physics have laid stress on other phenomena in which it is possible to observe only the initial and final states without being able to visualise the intermediate mechanism.

The fact that such a change can occur in the carbonyl compounds may also suggest by analogy that such primary reactions as :

$$\begin{array}{c} H \\ \diagdown \\ N—H \rightarrow H_2 + NH \\ \diagup \\ H \end{array}$$

$$\begin{array}{c} H \\ \diagdown \\ O \rightarrow H_2 + O \\ \diagup \\ H \end{array}$$
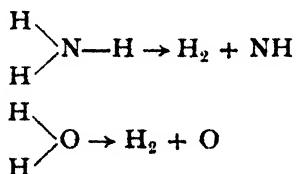
are not impossible. Goodeve and Stein have postulated the latter, and Mr. Gedye in his paper to be read later gives evidence of the participation of the NH radicle in the photosensitised decomposition of ammonia and also in the somewhat analogous decomposition by gaseous ions. It seems not improbable, therefore, that it might also occur as the primary change in the direct photochemical decomposition. It must be emphasised, however, that this is only a suggestion and requires further proof, while in the case of the carbonyl compounds this type of decomposition must be accepted as a fact.

Professor Mecke, in reply, wrote : I agree with Dr. Norrish that the decomposition of ammonia will proceed in very much the same way as the photochemical dissociation of carbonyl compounds ; both HCO and NH_2 are known to be very unstable compounds with low dissociation energies (*cf.* the remarks of Dr. Frankenburger on pages 409 and 478). But it is quite a different thing in the case of water. OH is a stable molecule with a rather high dissociation energy (106 cal.). It is found as a dissociation product in the thermal decomposition of water vapour and can be detected by decomposing water photochemically. The only possibility of explaining a dissociation process like $\begin{smallmatrix} H \\ H \end{smallmatrix}\!\!\!\searrow\!\!\!X = H_2 + X$ (*i.e.* the splitting up of two valence bonds and the formation of a new one by one act) is to assume very highly excited deformation oscillations, as I have called them, in which the two hydrogen atoms vibrate mainly perpendicular to the valence bond, approaching each other whilst the radicle X decomposes :
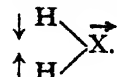
$\begin{smallmatrix} \downarrow H \\ \uparrow H \end{smallmatrix}\!\!\!\searrow\!\!\!\overrightarrow{X}.$ I do not like to accept this possibility until definite proof can be given that on irradiating H_2O with light of $\lambda 1800$, atomic oxygen is formed.

Dr. Helge-Petersen (*Copenhagen*) (*communicated*), said : Having had the good fortune to see the interesting communication of Professor Mecke on the formation of ozone in the upper layers of the atmosphere, I should be glad to be given room for the following statement.

In a recent issue of *Communications magnétiques*, etc.,[11] published by the Danish Meterological Institute, I have discussed the problem as to the nature of the different kinds of processes connected with the absorption of the solar radiation in the atmosphere, amongst these processes being that involving the formation of ozone. It appears from the investigation that such processes must invariably exhibit a maximum of intensity at a certain height, which depends on the physical state of the absorbing gas (temperature, etc.) and on the absorption coefficient of the effective radiation (wavelength). In particular, I would say that the resulting distribution of the ozone is only slightly different from that found by Mecke ; the distances below maximum density (of the densities 1/4 and 1/1000 of the maximal density) come out with a difference of only 1 to 2 km.

Furthermore, the value of the absorption coefficient for the light effecting the dissociation of O_2 (λ = about 1850 Å.), determined experimentally by Kreussler,[12] gives the height for the maximum of ozone density (the ozone layer) as 40 to 50 km., in good agreement with the observations. Moreover, it seems possible in accordance with this theory to account for the seasonal variation of the amount of ozone and its distribution over the earth.

S. Chapman[13] has treated the same problem in some recent treatises. Quite recently Götz und Ladenburg[14] seem to have brought forward evidence that ozone is also present, though in minute quantities, in the lower part of the atmosphere, in every case at heights of 2 to 3 km. ; they have found a perceptible ozone absorption over a horizontal distance of 4 to 5 km.

[11] *Communications magnétiques*, etc. nr. 13 : " A theoretical determination of the heights of the stratosphere, the ozone layer and the height of maximum luminosity of the aurora." By Helge-Petersen.

For readers interested in the matter, separate reprints of *Comm. magnét.* are available upon application to the Meteorological Institute, Copenhagen, so long as stock is available.

[12] *Handbuch der Experimentalphysik*, **19**, 287.

[13] *Mem. Roy. Meteorol. Soc.*, **3** (26), 1930 ; *Phil. Mag.*, **10** (Sept.), 1930.

[14] *Naturwiss.*, **18**, 1931.

Professor J. E. Lennard-Jones (*Bristol*), said : Professor Mecke has provided a very interesting suggestion as to the mechanism by which ozone is created and maintained at high altitudes. I should like to ask him whether he has considered the effects of the alternation of day and night, and whether or not he thinks ozone would be absent during the polar night. Meteorologists are, I believe, under the impression that there is little variation in the amount of ozone present by day and by night, and that the amount of ozone during the polar night is actually above the average for the whole world.[15]

I should like to congratulate Professor Mecke on his lucid and valuable introduction to this discussion.

Professor Mecke, in reply, said : I want to thank Dr. Helge-Petersen for referring me to his paper on this subject, which, I am sorry to state, had escaped my attention. The purpose of my paper (the full account of which will be published in the *Z. physik. Chem.*, Bodenstein Volume) was to discuss the photochemical equilibrium of ozone on the outline put forward in my introductory paper. In this paper I have calculated the height of the ozone layer, using the same value of absorption coefficient of oxygen (40-50 km.) as used by Dr. Helge-Peterson. But, of course, this will give only the order of this height, as we know nothing about the intensity distribution of sunlight in the far ultraviolet and of the absorption coefficients of oxygen for other wavelengths. Further I want to state here, that the height of the ozone layer must be different at the poles than at the equator on account of the different angles of incidence of the sunbeams. I expect the layer to be higher up in the atmosphere and to be thinner at the poles. I think the amount of ozone found in the lower part of the atmosphere (2×10^{-6}) is partly due to a number of ozone molecules which have dropped down by their own weight from the higher parts of the atmosphere, thus surviving their ultraviolet decomposition up there.

It is, of course, a serious objection, as stated by Professor Lennard-Jones, that ozone is very likely to be present in the atmosphere during the polar night. The means of explaining this fact, which ought to be investigated extensively, may be found rather in the very great stability of ozone in a thin atmosphere at low temperature, than in the possibility of transport by winds to the poles and in the formation by cathode rays, which are assumed to be especially strong near the magnetic poles. This process will practically follow the same rules as the formation by light.

[15] *Cf.* Dobson, *Proc. Lond. Phys. Soc.*, **43**, 339, 1931.

THE ABSORPTION SPECTRA AND THE OPTICAL DISSOCIATION OF THE HYDRIDES OF THE OXYGEN GROUP.

By C. F. Goodeve and N. O. Stein.

There has recently been considerable discussion among photochemists as to the validity of a quantitative application of the dissociation theory to photochemical processes. Franck[1] originally showed that in the case of chlorine, an elementary act of absorption resulted in dissociation at the

[1] J. Franck, *Trans. Farad. Soc.*, **21**, 536, 1926.

convergence limit of a discontinuous band system and beyond. This theory has been successfully applied to other substances.

In the case of heteropolar molecules, it is found that some exhibit discontinuous followed by continuous absorption, and some only continuous. It appears that ionically bound molecules predominate in the second class, and compounds which are close to each other in the periodic system predominate in the first group. For example, compounds such as HCl, and NaI, possessing ionic linkages, exhibit strictly continuous, while compounds such as NO, ICl, NaK, and LiH exhibit discontinuous spectra. A study of absorption spectra may offer a means of distinguishing between ionic and atomic linkages.

In the case of the alkali-metal halides, the thresholds of continuous absorption have been found by Terenin to be related to the heats of dissociation.[2] The legitimacy of the reverse calculation has been questioned by Bowen[3] but on correcting his values using more recent thermochemical data better agreements are indicated. Franck's dissociation theory has been extended and agreement with thermochemical data obtained with a number of triatomic molecules. The monoxides of nitrogen and chlorine show only continuous absorption, the latter exhibiting a sharp threshold corresponding to the dissociation energy of the molecule.[4] The dioxides of carbon, nitrogen, sulphur, and chlorine on the other hand show discontinuous absorption converging to a region of continuous absorption. Agreement of this limit with the thermochemical heats of dissociation has in most cases been found.

The present investigation was undertaken with the intention of obtaining further information with respect to tri-atomic molecules. The substances investigated were water, hydrogen sulphide, hydrogen selenide, and hydrogen telluride.

The Preparation of the Substances Investigated.

Hydrogen sulphide was generated from iron sulphide and passed into a suspension of magnesium oxide in water. The resulting magnesium hydrosulphide was subsequently heated and the evolved pure hydrogen sulphide was bubbled through water, dried over calcium chloride, condensed in liquid air, fractionated and dried over phosphorous pentoxide.

Hydrogen selenide was prepared by the action of water and dilute hydrochloric acid on aluminium selenide, which was formed by the action of the pure elements on each other. The gas was condensed in liquid air, and fractionated and dried over phosphorous pentoxide.

Hydrogen telluride was prepared in a similar manner to hydrogen selenide, but was even more thoroughly dried, since, as is well known, traces of moisture rapidly decompose it. When dried by passing it through a phosphorous pentoxide tube several times it was found to be sufficiently stable for the absorption measurements.

The Optical System.

The light sources used were a 100 C.P. " Pointolite " for the visible, a mercury arc lamp for the visible and near ultra-violet, a tungsten-steel spark and an aluminium spark for the far ultra-violet. The incident light was made parallel by means of a quartz lens. Two exactly similar absorption tubes were used in each experiment. The longer ones (235 and 25 cm.) were of glass with ground-on quartz windows, and the shorter ones (4 and

[2] A. Terenin, *Z. Physik*, **37**, 98, 1926.

[3] E. J. Bowen, *Trans. Farad. Soc.*, **21**, 543, 1926.

[4] C. F. Goodeve and Janet I. Wallace, *Trans. Farad. Soc.*, **26**, 254, 1930

1 cm.) were entirely of quartz, with plane parallel ends. One tube was used as a standard, and the other served to hold the gas under investigation. The absorption tubes were placed one above the other and were held parallel to each other and exactly horizontal by a rigid wooden structure which was itself fixed to an adapted cathetometer stand.

When the pointolite or the mercury arc was used as a source, the two parallel tubes were brought to such a vertical position as to make the incident beams of parallel light of equal intensity. A system of prisms brought the emergent beams into coincidence about two centimetres in front of the slit of the spectrograph. A quartz bi-prism affixed in front of the slit then made the two beams again parallel and also coincident. A comparison photograph was taken on every plate to test that the optical system was in correct alignment and that the two superimposed spectra
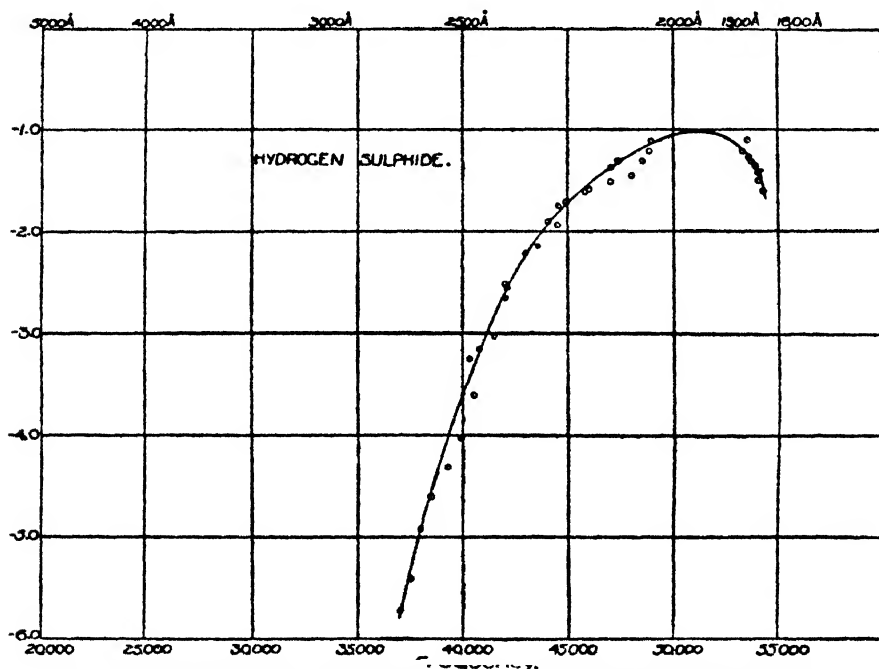
Fig. 1.—The extinction coefficients of Hydrogen Sulphide (ordinates $\log_{10} a$).

were of equal intensity. A similar test after each experiment showed that the amount of solid substance deposited on the window from the photo-decomposition of the gases was negligible.

When using the tungsten-steel and aluminium sparks, for work in the far ultra-violet, it was found impossible to obtain two parallel beams of equal intensity for all wavelengths, and it was, therefore, necessary to eliminate the prism system entirely. The comparison and gas-filled tubes were *successively* brought into optical alignment, by moving the rigid structure which supported both tubes, vertically up and down on the cathetometer stand. By exposing for exactly the same time, for each tube, perfect comparisons were obtained before each experiment.

Hilger spectrographs of three types were used: for the visible and near ultra-violet, a "wavelength" instrument with glass optical system, for the near ultra-violet a quartz E. 3 instrument, and for the far ultra-violet, a small quartz instrument of the E. 369 type. Schumann plates were used

at first for the far ultra-violet, but it was found that ordinary plates could be satisfactorily used with the aluminium spark.

The following procedure was carried out to determine the values of the extinction coefficients. The condensed gas was allowed to evaporate into one of the two absorption tubes which had previously been evacuated. The pressure of the gas was then reduced from one atmosphere to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, etc. atmospheres, the pressure being read on a direct reading manometer. Careful drying of the apparatus and the gas prevented corrosion of the manometric mercury. An exposure was taken at each pressure, with the light incident on the comparison tube reduced to one-half by means of a rotating sector. The match points were determined with the aid of a hand lens and their wavelengths measured. The value of a the extinction coefficient is given by,

$$ a = \log_{10} \frac{I_0}{I_T} \times \frac{1}{pl} = \frac{0.301}{pl}, $$

where p is the pressure in mm. of mercury and l the tube length in centimetres. A series of experiments were carried out with different tube
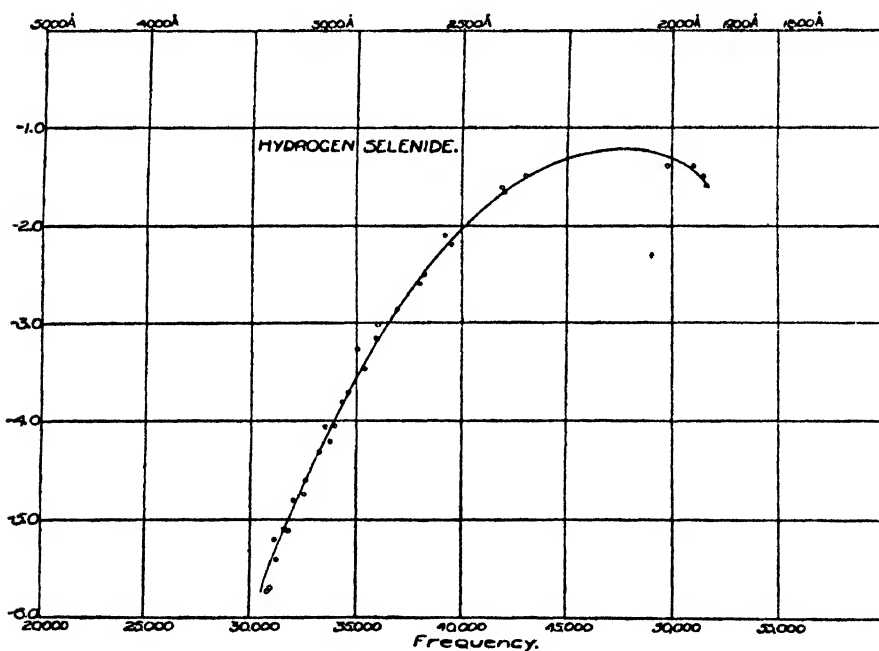
FIG. 2.—The extinction coefficients of Hydrogen Selenide (ordinates $\log_{10} a$).

lengths and fresh preparations of the gases. Curves were then plotted with the logarithms of a as ordinates and the corresponding frequencies as abscissæ.

In the experiments, the results of which are given below, no high degree of photometric accuracy was attempted. It is difficult to estimate the limits of error of the measurements, but from the reproducibility of the results it is considered that the maximum error in the values of $\log_{10} a$ is not greater than $\pm$ 0.1, and in some parts of the curves it is much less than this. The values of a are, therefore, probably correct to about 10 per cent. The curves may be used for the quantitative estimation of the gases studied with this accuracy.

Water.

Leifson [5] found water transparent to light down to 1830Å. but rapidly increasing in absorption beyond this point. The vapour showed a band from 1780Å. to 1610Å., with a maximum at 1700Å., and a second band commencing at 1392Å. Granath [6] measured the extinction coefficients of water vapour and found it to absorb weakly at 2000Å. but to rise to a steep threshold at 1850Å. (54,000 w.n.).

An attempt was made to confirm the above experimental results using liquid water in layers of 1 cm. to 35·5 cm. thickness. The values so obtained, calculated as if the water were a gas at room temperature are shown in Fig. 3. It appears as if the curve rises to a threshold beyond the
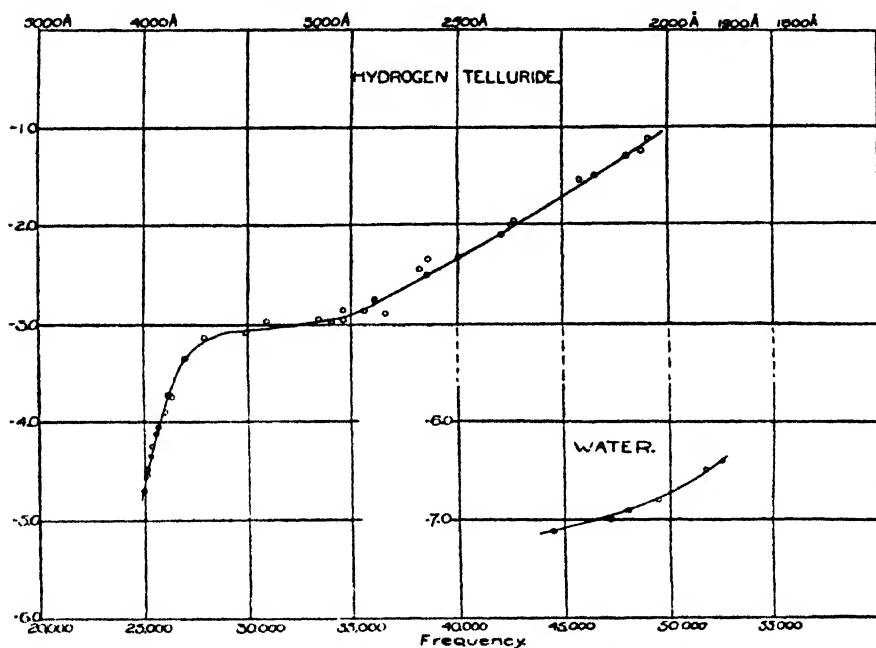
FIG. 3.—The extinction coefficients of Hydrogen Telluride and Water (ordinates $\log_{10} \alpha$).

range of our instruments in the neighborhood of 57,000 wave numbers (1750Å.). Although a high degree of purity of the water was attained, it is still possible that the absorption before the threshold is due to minute traces of impurities; or it may be due to association.

The heat of formation of water vapour from its elements is 58·3 Cals. The values for the heat of dissociation of the oxygen molecule have varied over a wide range in recent years, but Copeland [7] and Rodebush and Troxel [8] have independently, by direct calorimetric methods, obtained the same value, 131 Cals. A large number of optical and photochemical methods give values within ± 2 Cals. of this value. The value of 131 ± 2 Cals. can be taken as correct with a fair degree of certainty. McLennan and Crawford [9] have suggested that the difference between a normal and ^1D metastable

[5] S. W. Leifson, *Astrophysical J.*, **63**, 73, 1926.
[6] L. P. Granath, *Physical Rev.*, **34**, 1045, 1929.
[7] L. C. Copeland, *Ibid.*, **36**, 1221, 1930.
[8] W. H. Rodebush and S. M. Troxel, *J. Am. Chem. Soc.*, **52**, 3467, 1930.
[9] *Nature*, p. 874, 1929.

oxygen atom corresponds to 10,490 w.n. (30·0 Cals.). This value is confirmed by the fact that the difference between the convergence limit of the oxygen bands and the above heat of dissociation of oxygen, corresponds to 31 Cals. The heat of dissociation of water into a hydrogen molecule and a ^1D oxygen atom is therefore $154\cdot3\pm1\cdot5$ Cals. corresponding to $54,200\pm500$ w.n. The agreement of this value with the threshold of the water vapour absorption found by Granath (54,000 w.n.) would indicate that the dissociation of water into a hydrogen molecule and a ^1D oxygen atom can take place in this band.

Although only preliminary measurements have been made on the absorption of liquid water, they are sufficient to indicate that the threshold of absorption of the liquid lies some distance to the higher frequency side of the threshold of the vapour absorption. This is to be expected as 10 Cals. are required in addition on account of the heat of vaporisation of water. The threshold of absorption of liquid water, should, on the above basis, lie at 57,200 w.n. or 1750Å. Although the measurements shown in Fig. 3 are not sufficient to show the exact position of the threshold, yet, as far as they go, they are in agreement with this conclusion. It is furthermore of interest to note that the difference between the thresholds of the first and second bands of water vapour as found by Leifson (18,000 w.n.) is strikingly close to the difference between the ^1D and the ^1S levels (17,925 w.n.) suggested by McLennan and Crawford for oxygen. Photo-dissociation into a hydrogen molecule and a ^1S oxygen atom is therefore possible in this band.

There are two other methods of dissociation to be considered. Of these, complete dissociation into three atoms requires about 225 Cals. or light of 1280Å. to be absorbed. Dissociation into a hydrogen atom and a hydroxyl molecule requires only about 90 Cals.[10] The excess of 65 Cals. might be contained in the OH molecule but not sufficient is known about the molecule to decide whether this is probable or even possible.

A review of the literature shows several attempts to decompose water by ultra-violet light from a mercury arc lamp, and it is reported that hydrogen, oxygen, and hydrogen peroxide were obtained in measurable amounts with long exposures.[11]

The mercury arc, after short initial exposures, no longer emits light below 1950Å., and, as water vapour absorbs a negligible amount of light at and above this wavelength, it seems improbable that the direct decomposition of the water was effected by this means. These decompositions can be explained more simply as a photosensitisation by impurities or by the walls of the vessel. This is supported by the fact that Gaviola[12] has found water vapour to be decomposed with the production of hydroxyl molecules in the mercury-photosensitised reaction. Photodecomposition in the region of the first absorption band (1850Å.) does not appear to have been carried out. A preliminary attempt is being made in this laboratory.

Hydrogen Sulphide.

The absorption of light by hydrogen sulphide has been investigated by a number of workers,[13] but no definite information has been given. Liveing

[10] E.g. D. S. Villars, J. Am. Chem. Soc., 51, 2374, 1929.
[11] See Photosynthesis, Spoer, Amer. Chem. Soc. Monograph, pp. 301-303 and also Kernbaum, Compt. rend., 149, 273, 1909: Thiele, Z. angew. Chem., 22, 2472, 1909; Coehn, Ber. Chem. Ges., 43, 880, 1910; Berthelot and Gaudechon, Compt. rend., 150, 1690, 1910.
[12] E. Gaviola, Temas de Quim., 2, 173, 1929.'
[13] J. Tyndall, Phil. Trans. 152, 59, 1862; W. A. Miller, Phil. Mag. 4 (25), 304, 1863; P. Baccei, Nuovo Cimento (4), 9, 189, 1899.

and Dewar [14] state that "hydrogen sulphide produces complete absorption above wavelength 2580Å. (39,000 w.n.) and below that a partial general absorption." Ciechomski [15] found that the liquid absorbs partially the whole ultra-violet and completely the shorter wavelengths.

In the present investigation the extinction coefficients a were determined over a range of pressures, and thicknesses of layer, and their logarithms were plotted against the corresponding frequencies (Fig. 1). The absorption curve rises steeply to 42,000 wave numbers, beyond which it rises less steeply to a maximum at about 51,000 w.n. thence it decreases rapidly to the limit of the instrument, 54,000 w.n. With the longest tubes, and with a background of the continuous emission of the mercury arc, no discontinuous absorption could be found. The continuous absorption exhibits a threshold at 37,000 wave numbers.

The heat of dissociation of hydrogen sulphide is given by the equation. [16]

$$H_2S \text{ gas} \rightarrow H_2 + \tfrac{1}{2}S_2 \text{ gas} - 19\cdot610 \text{ Cals.}$$
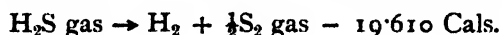
The heat of dissociation of $\tfrac{1}{2}S_2$, obtained from thermal equilibrium data is 62 Cals. (International Critical Tables) and from optical data 56 Cals. [17] Using the average of these values, 59 ± 3 Cals. and the value given by McLennan and Crawford [9] for the ^1D level of the sulphur atom (9200 w.n.), it can be shown that 105 ± 3 Cals. are necessary to dissociate hydrogen sulphide gas into a hydrogen molecule and a ^1D sulphur atom. This is equivalent to $37,000 \pm 1000$ w.n. which is in agreement with the threshold of absorption of hydrogen sulphide gas. Dissociation of hydrogen sulphide in this manner is therefore possible in this absorption region of the gas.

It is well known that dry hydrogen sulphide gas is decomposed by light of short wavelength. In our experiments, a deposit of sulphur was formed on the windows of the absorption tube which increased in density the longer the exposure to an intense ultra-violet source. The primary process of decomposition into hydrogen molecules and metastable sulphur atoms is evidently followed by recombination of the sulphur atoms on the walls of the tube and their association to solid sulphur.

There is still to be considered the possibility of dissociation into an HS molecule and a hydrogen atom. The energetics of such a dissociation cannot be calculated, but by analogy to water, it is probable that the energy required for such a dissociation is much less than that given by the threshold. HS molecules would probably combine to form hydrogen disulphide, which if formed in any quantity should have been detected in our experiments.

Hydrogen Selenide.

The absorption of light by hydrogen selenide has been studied in a purely qualitative way by Plücker. [18] In the present investigation the extinction coefficients were determined over a range of pressures and thicknesses of layer and their logarithms were plotted against the corresponding frequencies (Fig. 2). The absorption is strictly continuous and the curve rises steeply at first to 35,000 w.n., then less steeply to a maximum between 45,000 and 50,000 w.n., after which it again falls steeply. A threshold is exhibited in the neighbourhood of 32,000 w.n.

[14] *Chem. News*, **47**, 121, 1883.
[15] L. Ciechomski, *Diss. Freiburg University*, 1910.
[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," pp. 542, McGraw-Hill, 1923.
[17] B. Rosen, *Z. Physik*, **43**, 69, 1927.
[18] J. Plücker, *Pogg. Ann.*, **121**, 459, 1864.

Preuner and Brockmöller[19] calculated the value for the heat of dissociation of hydrogen selenide gas from thermal equilibrium data as,

$$H_2Se \text{ gas} = H_2 \text{ gas} + \tfrac{1}{2}Se_2 \text{ gas} - 22 \cdot 25 \text{ Cals.}$$
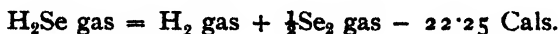
The optical value for the heat of dissociation of $\tfrac{1}{2}Se_2$ gas into a normal selenium atom is—42·0 Cals. Adding to these the energy of the metastable ^1D selenium atom, 23 Cals., it is found that 87·2 Cals. are required to dissociate hydrogen selenide into a hydrogen molecule and a ^1D selenium atom. This energy is given by light of and above 30,700 w.n. which point marks the beginning of the absorption of the gas.

Several investigators have shown that dry hydrogen selenide is decomposed by ultra-violet light.[20] In our experiments a deposit of selenium of the red amorphous variety was formed on the windows of the absorption tube during the exposures to light of short wavelength. It seems evident that, as in the case of hydrogen sulphide, the primary process of decomposition into hydrogen molecules and metastable selenium atoms is followed by recombination of the selenium atoms, probably on the walls, and their association to solid selenium.

Hydrogen Telluride.

There appears to have been no work recorded on the absorption of light by this substance, nor have accurate or consistent values for its heat of formation been given. In the present investigation the extinction coefficients were, as in the previous cases, measured over a range of thicknesses of layer and pressure (Fig. 3). The absorption is again strictly continuous, a threshold being exhibited in the neighbourhood of 25,000 w.n. The curve rises very steeply to about 30,000 w.n., shows a horizontal region between 30,000 and 35,000 w.n. then rises steeply again following almost a straight line path to the limit of the instrument.

It has been found that exposure of hydrogen telluride to a mercury arc produces a deposit of tellurium on the walls and windows of the absorption tube. If we can assume that the same primary optical dissociation takes place with this gas as was indicated with the other hydrides, a value for its heat of formation can be calculated from the threshold of absorption. The legitimacy of this calculation will be discussed below. Thus from the following equations,

$$H_2Te \text{ gas} = H_2 \text{ gas} + Te(^1D - 71 \cdot 3 \pm 1 \cdot 5 \text{ Cals. } (25,000 \text{ w.n.})$$
$$Te(^1D = Te \text{ normal} + 21 \cdot 1 \text{ Cals. } (7,406 \text{ w.n.})[9]$$
$$Te \text{ normal} = \tfrac{1}{2}Te_2 \text{ gas} + 32 \cdot 5 \text{ Cals.}[17]$$
$$\text{Hence } H_2Te \text{ gas} = H_2 \text{ gas} + \tfrac{1}{2}Te_2 \text{ gas} - 17 \cdot 7 \text{ Cals.}$$
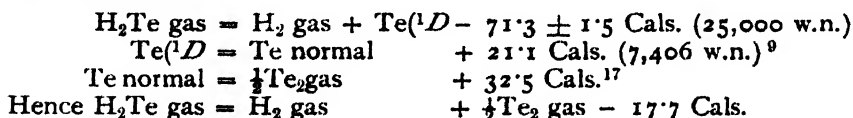
A value is obtained which is reasonable considering those of the other hydrides of this group.

Hydrogen telluride is distinct from the sulphide and selenide in that it shows what is apparently a second threshold, although this is much less steep than the first. This second threshold may mark the beginning of a region in which dissociation into different products takes place, and it is of interest to note that the difference $^1D - ^1S$ (12,640 w.n.)[9] corresponds approximately to the difference between the two thresholds as shown in

[19] G. Preuner and I. Brockmöller, *Z. physik. Chem.*, **81**, 129, 1912.
[20] R. de Forcrand and H. Fonzes-Diaczon, *Compt. rend.*, **134**, 171, 229, and 281, 1902; W. Hempel and M. G. Weber, *Z. anorg. Chemie*, **77**, 48, 1912; L. Moser and E. Doctor, *Z. anorg. Chem.*, **118**, 284, 1921.

Fig. 3. Dissociation with the production of metastable ^1S tellurium atoms is thus possible in this second absorption region.

Discussion.

On comparing the absorption spectra of the four hydrides of the oxygen group, it will be observed that they all exhibit thresholds or regions of rapidly increasing extinction coefficients. These threshold regions progressively shift towards lower frequencies as we go down the series from water, and, as shown above, the energy corresponding to these thresholds is just sufficient to dissociate the molecules into hydrogen molecules and ^1D non-metal atoms. Although photochemical evidence is insufficient at present to prove that such a dissociation does take place, such evidence as exists is in accordance with it.

In other respects hydrogen sulphide and selenide are the only two that show great similarity, but it is possible that further investigation with very great absorbing thicknesses and measurements beyond the limits of quartz instruments may show that all have essentially the same features. On the other hand the second thresholds found with water and hydrogen telluride and attributed to the production of the ^1S non-metal atoms do not occur with the other two gases, and in fact, the absorption rapidly decreases in the region where such a threshold would be expected.

A summary of the thermochemical and optical data is shown in Table I.

TABLE I.

	Water.	Oxygen.	Hydrogen Sulphide.	Sulphur.	Hydrogen Selenide.	Selenium.	Hydrogen Telluride.	Tellurium.
Thermochemical heat of dissociation.	$-58\cdot3$	—	$-19\cdot61$	—	$-22\cdot25$	—	$-17\cdot5$ (calc.)	—
½ heat of dissociation of diatomic molecule.	—	$-65\cdot5$	—	-59	—	-42	—	$-32\cdot5$
$^3P - {}^1D$	—	$-30\cdot5$	—	$-26\cdot2$	—	$-23\cdot0$	—	$-21\cdot1$
Thermochemical heat of dissociation into H_2 and ^1D atom.	$-154\cdot3$	—	-105	—	$-87\cdot2$	—	$-71\cdot1$ (assumed)	—
Corresponding frequencies.	54,200	—	37,000	—	30,700	—	—	—
Observed position of threshold.	54,000	—	37,000 to 38,000	—	31,000 to 32,000	—	25,000	—

The limits of error cannot in all cases be given even approximately and have been omitted.

The calculation of the heat of decomposition of hydrogen telluride raises an interesting point as to how accurate a measure the threshold of absorption is of the thermochemical heat of dissociation. Thresholds of absorption are not fixed points on the frequency scale, and the problem is,

what particular point represents the dissociation energy of a molecule having initially the average energy of the bulk, into molecules or atoms having the same kinetic energy, that is, the true heat of dissociation at the absolute zero.   This could be shown by a consideration of the usual curves[21] representing the potential energy of the molecule in the ground and in the excited levels, plotted against the distance between its atoms.   These may be of such a shape and in such a relative position that absorption of light can only take place with wavelengths that dissociate the molecule into parts with high kinetic energies.   In the case of the first three members of the group of compounds investigated, this is apparently not the case and the calculation of the heat of decomposition of hydrogen telluride is justified only if its potential energy-distance curves are similar to those of the other members.

The investigation has added to the already numerous examples of substances which show a relation between their thermochemical and optical properties.   It has not been attempted to give any theoretical explanation of this relation nor of why dissociation should take place in the manner indicated.   This must await a detailed examination of the chemical forces between the constituent atoms in their various electronic states.

The authors wish to express their thanks to Mr. S. Barratt for his kind criticism and advice, and to Professor F. G. Donnan for his interest in the work.

Summary.

The extinction coefficients of the hydrides of the oxygen group have been measured over a large range of pressures and thicknesses.   In each case an absorption curve has been plotted and the positions of the thresholds determined.   These positions have been found to agree with the thermochemical values of the heat of dissociation into normal hydrogen molecules and ^1D non-metal atoms.   The hydrides have been found to be decomposed photochemically in their absorption regions.   The thermochemical heat of dissociation of hydrogen telluride has been evaluated, assuming that the threshold of absorption of this substance corresponds to the same primary photochemical reaction as with the other hydrides.   The conditions involved in this assumption have been discussed.

[21] *E.g.*, E. V. Condon, *Physical Rev.*, **32**, 858, 1928.

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GENERAL DISCUSSION.

On Part I., Paper 3.

Dr. G. Herzberg (*Darmstadt*) (*communicated*) : It seems hard to believe that by light absorption, in one process, the normal H_2 molecule can be split off from these hydrides because the H-atoms are not bound together in them.   I rather think that the agreement of the threshold frequency with the energy necessary for that process is fortuitous.   Moreover, in the case of H_2O Goodeve and Stein use values for the heat of dissociation of O_2 and the energy of the metastable ^1D level of O, which

are no longer correct. Using the correct values [1] I get 163·3 Cals. for the process $H_2O \rightarrow H_2 + O(^1D)$ as assumed by Goodeve and Stein. This is much larger than the observed threshold 153 Cals. So, at least in this case, Goodeve and Stein's photochemical interpretation of the continuous absorption spectrum cannot be right. It seems to me pretty certain that this first continuous absorption spectrum of H_2O corresponds to the dissociation $H_2O \rightarrow H + OH$ (normal) [2] which according to Mecke requires about 112 Cals. The excess energy of 40 Cals. for the threshold and 55 for the maximum of continuous absorption may well be translational energy of the products of dissociation. In the case of the methyl halides Scheibe and myself [3] definitely found translational energies of this same order of magnitude. It seems also plausible, when we consider the large width of this continuous spectrum, which points to the fact that the potential curve of the upper state is very steep. Of course part of the excess energy may also be vibrational energy of the OH-radical. The electronic excitation is too high (92 Cals.). Mecke in his paper has already explained the second continuous absorption of H_2O found by Leifson by the dissociation $H_2O \rightarrow H + OH$ ($^2\Sigma$ excited). The continuous absorption spectra of H_2S, H_2Se and H_2Te are presumably to be explained in a similar way. The formation of S in consequence of light absorption, as found by Goodeve and Stein, can then be explained by the process $HS + HS = H_2S + S$. I might add that I am just preparing to investigate the absorption spectra of these and other simple polyatomic molecules in the near and far ultraviolet (Schumannregion) with high dispersion and if necessary with very long absorption tubes.

Mr. C. F. Goodeve (*communicated*): I consider Dr. Herzberg's criticism most important. It is hoped that a study of the photodecomposition of these hydrides at present being attempted will give indications as to the nature of the primary process. I do not agree that our present knowledge of molecular structure and of continuous absorption is sufficient to permit of a decision being made between the suggestion of Dr. Herzberg and that given in our paper. Using the more recent value for the heat of dissociation of oxygen, the energy required for the dissociation, $H_2O \rightarrow H_2 + O(^1D)$, becomes 162 Cals. or 57,000 wave-numbers which still lies in the threshold region as found by Leifson. The absorption of light at frequencies below this may be due to association or to molecules already possessing a high energy content. The need for more experimental evidence is apparent.

Professor A. J. Allmand (*London*) said : I may remark that Tian published in 1916 an account of experiments on the photo-decomposition of water by light in the neighbourhood of 185 $\mu\mu$. The products were hydrogen peroxide and hydrogen, the latter not being formed if oxygen were present. The reaction went in the light from an aluminium spark discharge, but not in the light from an overloaded mercury lamp or in that from a zinc spark (not below 203 $\mu\mu$). With reference to the paper of Professor Mecke, experiments made in the King's College laboratory, both with filtered light [4] and with spectrally dispersed light [5] have convinced me that the $H_2 - Cl_2$ reaction takes place in the light of the mercury green

[1] Heat of dissociation of O_2 118 Cals. (Frerichs, *Physical Rev.*, **36**, 398, 1930; Herzberg, *Z. physik. Chem.*, B **10**, 189, 1930), energy of metastable O ^1D 46 Cals. (Frerichs *l.c.*).
[2] This was already suggested by G. Scheibe and myself in our paper on the methyl halides (*Zs. f. phys. Chem.*, B **7**, 390, 1930).
[3] See ref. 1.   [4] Published work of E. Beesley.
[5] Unpublished work of J. B. Bateman.

line (546 $\mu\mu$), a region so far removed from the convergence limit of the chlorine band-spectrum as to exclude the possibility of the dissociation of the Cl$_2$ molecule. Professor Mecke has mentioned the possibility of the existence in the molecular spectra of the halogens of metastable levels. It would be of much interest to know whether there are any present indications whatever of such metastable levels and, if not, whether there is any particular spectral region which would be more likely to contain them than others.

Professor Mecke said : The existence of metastable levels is probable at least in the case of iodine. By the investigations of Pringsheim and Rosen [6] we know now that there are four absorption spectra of iodine : the well-known red-green absorption, two absorption spectra in the ultra-violet below $\lambda 2000$ and a very faint one in the far red ($\sim \lambda 8000$). I believe that this later belongs to a metastable level and might be of some importance in photochemical work. There are no such spectroscopic indication in the case of chlorine, but it would be very advisable to look for them.

Mr. N. O. Stein (*London*) (*communicated*) : In reply to Professor Allmand's remark on the work of A. Tian [7] I wish to state that I have attempted to repeat Tian's results with a simple apparatus. Very pure water was placed in a quartz vessel, which had plane parallel windows about 1 mm. in thickness, and which was designed so that any gas evolved could be collected. This vessel was illuminated by a very intense condensed spark discharge between aluminium electrodes for over ten hours, at a distance of 2 cms. No gas was evolved, and on testing the water for hydrogen peroxide with titanium sulphate in sulphuric acid, none was found present. The decomposition found by Tian might have been due to a photosensitisation.

[6] *Z. physik,* 50, 1, 1928.   [7] A. Tian, *Ann. Physique,* 5, 248, 1916.

THE PHOTOCHEMICAL PROPERTIES OF THE CARBONYL GROUP.

By F. W. Kirkbride and R. G. W. Norrish (*Cambridge*).

During the last twenty years, a considerable amount of work has accumulated on the photolysis of aldehydes and ketones. The earlier work of Berthelot and Gaudechon [1] who studied formaldehyde, acetaldehyde, acetone, and several aldoses and ketoses shows that when the full radiation of the mercury vapour lamp is employed, the products may sometimes be complex (due largely to polymerisation), but they always obtained the evolution of carbon monoxide in large quantities, while carbon dioxide and hydrogen when produced (with the exception of glucose and maltose) were only formed to a very much smaller extent.

All these compounds have an absorption region with a maximum intensity near 280 $\mu\mu$ and Henri ascribed this band to absorption of light by the :CO group in the molecule. Henri and Wurmser [2] showed that

[1] Berthelot and Gaudechon, *Compt. rend.,* 151, 478, 1910, etc.
[2] Henri and Wurmser, *ibid.,* 156, 230, 1913.

acetaldehyde is decomposed by light of wavelength corresponding to this region, but not by light corresponding to the second region of absorption which begins about 220 $\mu\mu$, and Berthelot and Gaudechon [11] further showed that the sole products of decomposition in this region are methane and carbon monoxide

Very similar results are obtained when other carbonyl substances are irradiated with light absorbed by the carbonyl group : formaldehyde gives carbon monoxide and hydrogen with only a very small quantity (if any) of carbon dioxide and methane ;[3] acetone yields carbon monoxide and ethane and a very small amount of methane.[1] The ketoses dihydroxyacetone, erythrulose, lævulose, sorbose and perseulose give carbon monoxide and the corresponding alcohol containing one carbon less than the sugar is formed.[4]

A general survey of these decompositions leads one to the view that in all cases we can express the main reaction which occurs to some 90 per cent. at least by the general equations :

$$\begin{array}{c} R_1 \\ \diagdown \\ \diagup \\ R_2 \end{array} CO \rightarrow R_1R_2 + CO \text{ and}$$

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ H \end{array} CO \rightarrow RH + CO.$$
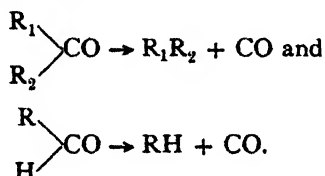
In the case of α-dicarbonyl compounds such as glyoxal, methyl glyoxal, and dimethylglyoxal, the region of absorption by the carbonyl groups is moved, by reason of the conjugation of double bands, into the visible part of the spectrum, and we now find that decomposition occurs in blue and violet light. The case of glyoxal vapour was investigated by Norrish and Griffiths,[5] who showed that here again the main products of decomposition—to the extent of 97 per cent.—are carbon monoxide, and a solid product consisting of glycerosone, whose constitution was fully verified.

$$2 \begin{array}{c} CHO \\ | \\ CHO \end{array} \rightarrow CO + \begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ CHO \end{array}$$
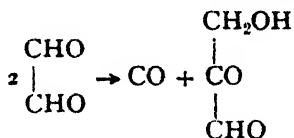
Some 2 per cent. of hydrogen was also obtained. The case of methyl-glyoxal vapour has been investigated by us with results quite analogous to that of glyoxal, the products obtained being carbon monoxide to the extent of 94 per cent. and a solid product $C_6H_8O_3$ which behaves exactly as the dimethyl derivative of glycerosone :

$$\begin{array}{c} CH_3 . CH . OH \\ | \\ CO \\ | \\ CH_3 . CO. \end{array}$$
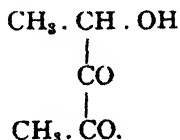
A similar experiment with dimethylglyoxal gave carbon monoxide to the extent of 86 per cent. and a residue whose constitution was not determined.

[3] Bredig and Goldberger, Z. physikal. Chem., 110, 532, 1924,
[4] Berthelot and Gaudechon, Compt. rend., 155, 401, 1912.
[5] Norrish and Griffiths, J.C.S., 2829, 1928.

It would therefore appear that these dicarbonyl compounds fall into line with the general scheme given above, in that the first action of the light is the elimination of carbon monoxide, but that, since there still remains a reactive : CO group in the residue a further secondary reaction may ollow, in accordance with the equations :

$$\begin{array}{ccc} R \cdot CO & & R \cdot CO \\ | & \rightarrow & | & + CO \\ R \cdot CO & & R \end{array}$$

$$\begin{array}{ccc} R \cdot CO & & R \cdot CO \\ | & + & | & \rightarrow R_4 C_3 O_3. \\ R & & R \cdot CO \end{array}$$
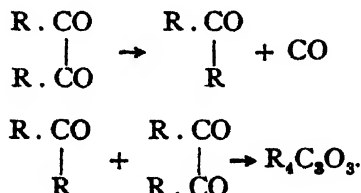
Further development in the study of the photochemical properties of carbonyl compounds has consisted mainly in the correlation of their photochemical and spectroscopic data.

De Hemptinne [6] showed that benzaldehyde is decomposed into benzene and carbon monoxide in accord with the scheme suggested above, but only by light of wavelength shorter than the point in the spectrum where predissociation starts, which at 20° C. is about 2550 AU. Henri has stated that acetaldehyde behaves similarly in this respect.[7]

In order to test further the general applicability of this view, we first examined the absorption spectra of glyoxal [8] and dimethylglyoxal vapour,[9] and also photographed and examined that of methylglyoxal vapour. The latter spectrum resembles the two former, and consists of a series of bands ranging from 4560 AU to an indefinite limit in the near ultraviolet. As far as 4378 AU the bands are fairly sharp, and often bands as close together as 2 AU could be separately measured. Beyond 4290 AU they became broader and so diffuse and faint that their positions could not be measured with any accuracy. This behaviour suggests that the molecule exhibits predissociation in this region where it is photochemically decomposed, but we have not been able to come to any definite decision on this point, because the transition from sharp to diffuse bands is gradual, and because we did not succeed in resolving any of the sharper bands into rotational lines. Similar difficulties appear to be experienced with the spectrum of dimethylglyoxal, and seem to be inherent in the problem, since in view of the large moments of inertia of these molecules the rotational separation is likely to be very small.

To study more effectively the relation between predissociation and photochemical change, we have examined further the photolysis of gaseous formaldehyde, for which the absorption spectrum has been fully worked out by Henri and Schou.[10] The band spectrum extends from 370 $\mu\mu$ to 250 $\mu\mu$, but from 270 $\mu\mu$ to 250 $\mu\mu$ the bands are diffuse and show no rotational fine structure. In our case the photochemical decomposition occurred practically quantitatively to carbon monoxide and hydrogen, and we were unable to confirm the formation of carbon dioxide or methane reported by Bredig and Goldberger.[3] Using a plate of " Vita-glass " 4 mm. thick as a light filter, we found a sharp photochemical threshold between 280 $\mu\mu$ and 265 $\mu\mu$. We therefore conclude that the case of formal-

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[6] De Hemptinne, *J. Physique et Radium* (VI.), **9**, 357, 1928.
[7] Henri, *Trans. Far. Soc.*, **25**, 765, 1929.
[8] Luthy, *Z. physikal. Chem.*, **107**, 302, 1923.
[9] Light, *ibid.*, **112**, 414, 1926.
[10] Henri and Schou, *Z. Physik*, **49**, 774, 1928.

dehyde is another in which the photolysis is limited to the region of predissociation.

If these results for benzaldehyde, formaldehyde and acetaldehyde be generalised, it would appear that the decomposition of the carbonyl compound occurs in one primary act, following the light absorption. This might take place in three ways :—

$$(1) \quad \begin{array}{c} R' \\ \diagdown \\ R'' \diagup \end{array}\!\!CO + h\nu \quad = CO + R' + R''$$

$$R' + R'' \qquad\qquad \rightarrow R'R' + R'R'' + R''R''.$$

$$(2) \quad \begin{array}{c} R' \\ \diagdown \\ R'' \diagup \end{array}\!\!CO + h\nu \quad = R'CO + R''$$

$$R'' + \begin{array}{c} R' \\ \diagdown \\ R'' \diagup \end{array}\!\!CO \quad \rightarrow R''R'' + R'CO$$

$$R'' + \begin{array}{c} R' \\ \diagdown \\ R'' \diagup \end{array}\!\!CO \quad \rightarrow R'R'' + R''CO$$

$$R'CO + R''CO \quad \rightarrow R'R' + R''R'' + R'R'' + CO.$$

$$(3) \quad \begin{array}{c} R' \\ \diagdown \\ R'' \diagup \end{array}\!\!CO \qquad\qquad = R'R'' + CO.$$
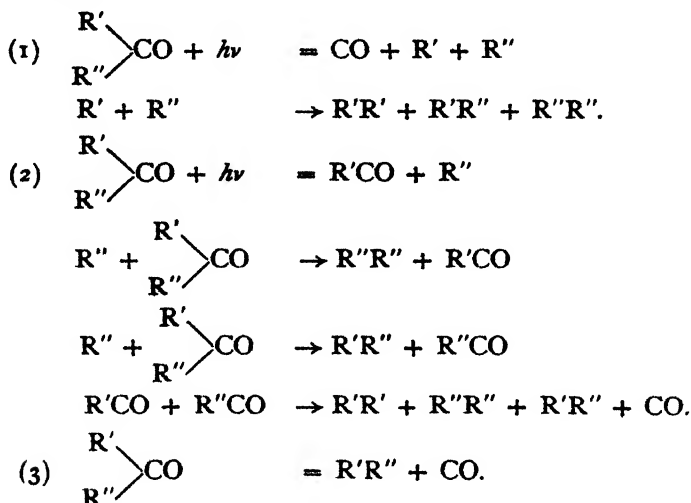
So far as acetaldehyde, formaldehyde, and benzaldehyde are concerned, it can be shown that the quantum of active light is of the right order of magnitude for the energy change involved in the primary process of (1). Therefore since the net reaction

$$\begin{array}{c} R \\ \diagdown \\ H \diagup \end{array}\!\!CO = CO + RH$$
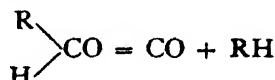
involves practically no energy change, the photoactive quantum should correspond to the heat of dissociation of the product RH into R and H. This is very approximately true for the three examples cited and was first shown for benzaldehyde by de Hemptinne, but it seems difficult to sustain for the dicarbonyl bodies which are decomposed by the much smaller quanta of blue light.

Further, it will be seen that both mechanisms (1) and (2) should give rise to a mixture of hydrocarbons when R' and R'' are different. Thus benzaldehyde should yield benzene, diphenyl and hydrogen, while acetaldehyde should give methane, ethane, and hydrogen. In practice we find that benzene[7] and methane[11] respectively are practically the only hydrocarbons produced. Similarly, a number of different alcohols should be obtained by the photolysis of a ketose, whereas it appears that only one alcohol is obtained from each sugar.[4] Again, in the decomposition of glyoxal and methylglyoxal, hydrogen is not produced to an extent greater than 2 per cent., and it may well be derived by secondary photolyses of the solid products, which are alcoholic in character. Such changes as

$$\begin{array}{ccc} R \cdot CO & & R \cdot CO \\ | & \rightarrow R + & | \\ R \cdot CO & & \cdot CO \end{array}$$
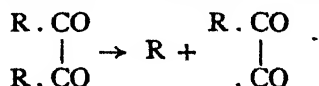
[11] Berthelot and Gaudechon, *Compt. rend,* **156,** 68, 1913.

therefore again appear unlikely. This is particularly so since the solid product of the change appears to consist almost entirely of glycerosone or its methyl derivative, which could hardly be the sole product of radicles of the type depicted above were present.

We are, therefore, led to the view that if photolysis occurs in one act, it is best represented by equation (3) above in which a molecule of CO is eliminated bodily from the molecule, and the remaining radicles combine together without separating.

This process should lead to a quantum efficiency of unity. Bowen and Watts [12] obtained a value of 2 for the decomposition of acetaldehyde, and we have obtained values between 1 and 2 for formaldehyde, but accurate results in both these cases are difficult to obtain owing to errors due to polymerisation. We may further note that as mentioned above, the reaction

$$\begin{array}{c} H \\ \diagdown \\ \diagup \\ H \end{array} CO = H_2 + CO$$
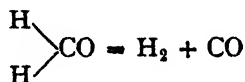
occurs practically without energy change, so that practically the whole of the energy of the absorbed quantum will appear in the products, which may therefore be capable of activating the reactants to some extent and so raising the quantum efficiency.

Summary.

A review of various examples of the photochemical decomposition of aldehydes and ketones, and an account of some new work on the decomposition of methyl glyoxal and formaldehyde are given. It is pointed out that decomposition giving carbon monoxide always ensues when absorption occurs in the "CO band" common to aldehydes and ketones which lies between 3500 and 2500 ÅU. This decomposition has been associated with a region of predissociation in the benzaldehyde spectrum by de Hemptinne, and also in the present work in the case of formaldehyde. Data are insufficient to establish it for other cases.

From a survey of the facts it is concluded that the primary change is best represented by the scheme

$$\begin{array}{c} R' \\ \diagdown \\ \diagup \\ R'' \end{array} CO = R'R'' + CO$$
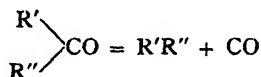
in view of the fact that the chief product is always $R'R''$. The substances $R'R'$ and $R''R''$ are, when formed, only very secondary products.

[12] Bowen and Watts, *J.C.S.*, **129**, 1607, 1926.

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GENERAL DISCUSSION.

On Part I., Paper 4.

Dr. W. Frankenburger (*Ludwigshafen*) said : The results which Messrs. Kirkbride and Norrish put forward seem to me to prove beyond question that in the photochemical decomposition of carbonyl compounds both the atoms or radicles attached to the carbonyl group of a molecule are affected practically simultaneously, or at any rate so quickly one after

the other that it is very much more probable that they will combine with one another rather than with atoms or radicles derived from a different molecule. We should expect that in the case of formaldehyde photochemical decomposition would give practically only H_2 and CO and that no glyoxal (resulting from two HCO radicles) would be formed since in this decomposition the life-period of the HCO radicle would be very short. It is perhaps of interest in this connection to refer to the results of experiments[1] on the *formation* of carbonyl compounds from H atoms and CO. These show that in addition to formaldehyde considerable quantities of glyoxal result from the reaction between hydrogen atoms (photochemically produced by resonance rays) and CO ; the proportion of these products in relation to the quantity of H atoms utilised leads to the conclusion that in this case the reaction process goes through the radicle HCO. From this the combination of two HCO radicles (to form glyoxal) seems to be at least as likely as the addition of a second hydrogen atom to HCO according to the scheme HCO + H → H_2CO. We may even presume that H_2CO is less likely to be formed in this way than to be produced in a secondary fashion from the glyoxal molecules (by virtue of the recombination energy they possess), according to the scheme[2] $H_2C_2O_2 \rightarrow H_2CO + CO$. Moreover our experiments accord with the conclusions which Mecke has drawn from spectroscopic data that the HCO radicle has a high sensitivity to temperature (small heat of formation) ; this may perhaps explain why in the *decomposition* of the H_2CO molecule, which requires a considerable amount of energy, the HCO radicle has a considerably shorter life period than in the corresponding combination reaction.

Dr. R. G. W. Norrish (*Cambridge*), in reply, said : I am grateful for the confirmatory evidence that Dr. Frankenberger has brought forward. The fact that the radicle HCO polymerises to glyoxal makes it improbable that these radicles and therefore H atoms figure in the direct decomposition of formaldehyde, since no glyoxal is produced in these circumstances. The products of the photochemical change appear to be solely H_2 and CO, the slow polymerisation of the formaldehyde which occurs in the dark being apparently unaffected by light.

[1] W. Frankenburger, *Z. Elektrochem.*, **36**, 757, 1930.
[2] Compare the suggestion of Professor Bodenstein for the oxidation of acetylene.

PART II. PHOTOCHEMICAL KINETICS IN GASEOUS SYSTEMS.

INTRODUCTORY ADDRESS.

By Professor Max Bodenstein (*Berlin*).

(*Delivered on* 17*th April*, 1931.)

The kinetics of photochemical processes are composed of two parts : the primary act which is immediately concerned with the absorption of a quantum of light and, secondly, the succeeding reactions which the products of this first act undergo.

The progress with regard to the act of absorption and its immediate consequences has been very remarkable since the last photochemical meeting of the Faraday Society, as has been indicated by the excellent report of

Professor Mecke. Our knowledge of the laws governing the succeeding reactions—which, of course, are merely dark reactions—has not made any fundamental progress in the meantime. On the other hand, this knowledge is not used as extensively—or as intensively—as it should be in the discussion of photochemical processes.

For this reason I propose to report very briefly upon the method of calculation using such laws. The first step involves an assumption as to the individual reactions which make up the process as a whole ; this assumption is now very greatly facilitated by the knowledge, as to the primary process, derived from spectroscopical investigations. The products of this primary process, which are practically never stable substances—they are excited molecules, atoms, or radicles—undergo further changes. Thus they have a short life ; a very short life, when compared with the time we need for our observations of the whole reaction.

It is, therefore, possible to assume the existence of a stationary state, in which the extent of the formation of these intermediate substances is, at any moment, as great as that of their consumption ; or in other words of a state in which the concentration of these substances does not change. This stationary state is, of course, short in comparison with the whole duration of the reaction. Moreover, an appreciable time must elapse before it is established after the beginning of the illumination ; this time is normally very short but in some cases may be measurable. During this time the concentration of the intermediate substances increases.

After having fixed the assumed partial reaction we can, by the use of the normal equations of chemical kinetics, write as many equations as there are unknown concentrations of intermediate substances, and therefrom resolve the whole system of equations. Let us take as an example of the atom chain for the hydrogen-chlorine reaction as suggested by Nernst. Its single reactions are :—

$$(1) \ Cl_2 + E = 2Cl$$
$$(2) \ Cl + H_2 = HCl + H$$
$$(3) \ H + Cl_2 = HCl + Cl$$
$$(4) \ Cl + Cl = Cl_2.$$
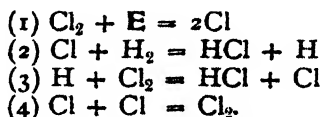
Here instead of (4) we could take $H + H = H_2$, $H + Cl = HCl$, but for the sake of showing the procedure of calculation we will use exclusively reaction (4).

In this case the formation of HCl is

$$\frac{d[HCl]}{dt} = k_2 \cdot [Cl] \cdot [H_2] + k_3 \cdot [H] \cdot [Cl_2].$$

The concentration of H and Cl are found by the equations :

$$\text{I.} \quad \frac{d[Cl]}{dt} = 2 \, I_{abs.} - k_2[Cl][H_2] + k_3[H][Cl_2] - k_4[Cl]^2.$$

$$\text{II.} \quad \frac{d[H]}{dt} = k_2[Cl][H_2] - k_3[H][Cl_2].$$

Putting both these velocities as equal to zero, we derive by addition of I. + II.,

$$2 \, I_{abs.} - k_4[Cl]^2 = 0$$

$$Cl = \sqrt{\frac{2 \, I_{abs.}}{k_4}}$$

II. gives

$$[H] = \frac{k_2[Cl][H_2]}{k_3[Cl_2]}$$

hence

$$H = \frac{k_2[H_2]}{k_3[Cl_2]} \sqrt{\frac{2 k_2 I_{abs.}}{k_4}}$$

wherefrom

$$\frac{d[\text{HCl}]}{dt} = k_2[\text{Cl}][\text{H}_2] + k_2[\text{H}][\text{Cl}_2] = 2k_2[\text{H}_2] \cdot \sqrt{\frac{2k_2 I_{\text{abs.}}}{k_4}}$$

This calculation is used merely as an example. We know that the velocity law thus derived does not hold good at all : the assumption we have made as to the individual steps of the reaction has been wrong.

In this way it is possible to exclude with all desired certainty some of such assumptions. But we are not in a position to say that those assumptions which lead to a velocity law in agreement with the observed facts is certainly right. For the hydrogen-chlorine reaction I assumed—in 1913— that the primary act is an ionisation of the chlorine molecule,

$$\text{Cl}_2 + \text{E} = \text{Cl}_2{}^+ + \theta.$$

I ought to have known even then, that this was impossible—I did not. Later in 1916 I suggested an excited molecule of chlorine,

$$\text{Cl}_2 + \text{E} = \text{Cl}_2{}^*.$$

At that time the heat of dissociation of chlorine was thought to be something of the order of 100,000 cal., so that visible light would be unable to split it.

Later Miss Cremer has operated with Cl_3 and Cl^* and all these intermediate products have given velocity equations agreeing with the facts as well as the simple atom chain of Nernst does, if one assumes that the end of the chain is not a recombination of the atoms, but a reaction of them, especially a reaction of H, with oxygen.

All those agree with a great number of facts and therefore it is impossible to say which is best. The number of facts must be increased more and more, and it will then be possible to exclude more and more assumptions and then finally to be lead to one single conception which really gives agreement with all the observations. This finally may be proved by calculating (or rather estimating) all the velocity-constants involved; these must, of course, have reasonable values which are as far as possibly in agreement with those deduced from similar reactions.

Thus in the case of chlorine and hydrogen I hope to show in my special paper that all the assumptions used up to the present time for the kinetics of the reaction are excluded by the sum of all facts observed.

It is, of course, a very long and a rather unsafe way of studying the mechanism of these reactions, to do so exclusively by kinetical measurement. I need not repeat, however, that for photochemical processes spectroscopy proves of great assistance, giving nowadays a nearly precise decision as to the primary process. In a few cases some help may be drawn from the fact that the intermediate products may give rise—in side-reactions—to substances which can be isolated, substances which are known or, may be, at the present time, unknown. In this manner we could practically assure ourselves of the intermediate existence of ClO_3 (in the decomposition of ClO_2 or O_3 in presence of Cl_2) by isolating its association product Cl_2O_6. Or the substances assumed may be such as are well known elsewhere : we can prove then whether an addition of these latter has the expected effect. Spectroscopy may help in yet another way by allowing us sometimes to detect the lines or bands of the intermediate substances in the reacting system, or it may give us proof that there are radicles whose existence is not improbable. An example of the first case we may take ClO_2 as found by its bandspectrum on decomposing Cl_2O, for the latter case COCl, the

substance which is converted into $COCl_2$ by Cl_2 or into CO_2, by O_2, for the existence of which especially Mecke has given spectroscopical reasons.

By these means one has calculated a great number of reactions, photochemical as well as dark reactions, long chains and short ones; even such photochemical processes in which the yield is in the closest possible connection with the Einstein law—as is the decomposition of hydrogen iodide or hydrogen bromide as investigated by Emil Warburg—or reactions in which this yield is far below one—for instance the oxidation of quinine by a more or less insufficient concentration of chromic acid, as measured by Luther and Forbes and calculated by myself. These calculations have frequently not been extended as far as was necessary and possible; in other words one has derived from them velocity laws which do not agree with all the observed facts but only with a part of them—even the hydrogen-chlorine reaction seems to me an instance of this. Without doubt, however, this method has lead, when properly applied, to a remarkable extension of our knowledge of the intimate mechanism of the chemical reactions, and I think one can say that when applied to photochemical processes their analysis and especially the fixation of their behaviour in relation to the Einstein law would hardly have been possible without it.

It seems to me, therefore, a rather surprising fact that it has been attacked very forcibly by Skrabal. When I used it first in 1913 I did not write

$$-\frac{d[H]}{dt} = k_n . C_1 . C_2 - k_m . C_3 . C_4 \ldots . = 0$$

but I said the velocity of the consumption of the intermediate substances is as great as that of their formation. We can therefore put the absolute value of the former equal to that of the latter,

$$k_n C_1 . C_2 = k_m . C_3 . C_4.$$

This has been transformed by Skrabal into: Bodenstein puts $+\dfrac{dH}{dt}$ equal $-\dfrac{dH}{dt}$

which, of course, is only possible if both are zero. I at once answered these attacks of Skrabal by showing the principle of the procedure, but I did not succeed in converting him and he has repeated his attacks.

I shall not go into details of this discussion. I only want to draw attention to the fact that it has even been possible, in a special case, to determine the velocity of the establishment of the stationary state and the stationary state itself, in perfect analogy with those calculations which determine the velocity with which an equilibrium is formed, as well as describing the equilibrium itself.[*] There are also, as may easily be imagined, cases in which it has not yet been possible to make such a calculation. That will happen when the stationary state is not established during the mean time of the process, if the concentration of the intermediate substances may be assumed never to be "constant." The thermal decomposition of ClO_2 as well as that of Cl_2O seem to be examples of such cases. Let us hope that even in these instances which show some rather extraordinary features we shall soon succeed in finding a way to describe these processes.

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[*] Bodenstein, Paddelt and Schumacher, *Z. physik. Chem.*, B. 5, 209, 1829. I ought to say that this calculation is due to Schumacher.

SOME REMARKS ABOUT „CHLORKNALLGAS."

By Professor Max Bodenstein (*Berlin*).

On the occasion of the last photochemical meeting arranged by the Faraday Society in 1925 one of our colleagues stated : " for the photochemical union of hydrogen and chlorine every author has his own mechanism." In the meantime the number of investigations has increased to a remarkable extent, but even now—when we are about to celebrate the eightieth anniversary of the first of these investigations by Bunsen and Roscoe—the problem is far from being solved and every new investigation produces further problems, as for instance the decreasing of the quantum yield with shorter wavelengths, as observed recently by Allmand.[1]

The assumption which has so far been used with the greatest success for the interpretation of the observed facts is that of the atom chain. If one realises that the chain may be broken by various reactions a good number of different velocity laws are derivable which agree with those experimentally determined. The individual steps of this chain are as follows :—

$$
\begin{aligned}
&(1) \quad Cl_2 + E = 2Cl \\
&(2) \quad Cl + H_2 = HCl + H \\
&(3) \quad H + Cl_2 = HCl + Cl \\
&(4) \quad H + O_2 = \ldots \\
&(5) \quad Cl + O_2 = \ldots \\
&(6) \quad Cl + X = Y \text{ or } Cl \rightarrow \text{walls} = \tfrac{1}{2}Cl_2
\end{aligned}
$$

Reaction (6) may be a diffusion of chlorine-atoms to the walls, followed by an adsorption and recombination, or it may be a reaction with a contaminating substance X as suggested in a newer investigation by Bodenstein and Unger [2] made with gases specially freed from oxygen.

If the chains end at reactions (4) and (5), and if their velocity is assumed to be proportional to $[H_2] . [O_2]$ and $[Cl_2] . [O_2]$, respectively, the law of the whole reaction is

$$
\frac{d[HCl]}{dt} = \frac{4k_2 . k_3 . I_{abs.} . [H_2] . [Cl_2]}{[O_2] . (k_2 . k_4 . [H_2] + k_3 . k_5 . [Cl_2])}.
$$

This equation, with $k_2 . k_4 : k_3 . k_5 = 10 : 1$, holds good for the experimental results with all concentrations varied over wide ranges, as shown especially by Thon.[3]

If the end of the chains in oxygen free gases is a reaction 6 the velocity is given [2] by

$$
\frac{d[HCl]}{dt} = \frac{4k_2 . I_{abs.} . [H_2]}{k_6[X]}.
$$

If finally there is a very small content of oxygen (or in the case of more oxygen, a more noticeable content of such a contamination as may react

[1] *J. Chem. Soc.*, 2709, 1930.
[2] Bodenstein and Unger, *Z. physik. Chem.*, B 11, 253, 1931. Y was assumed to be a chloride of silicon, formed by the reaction of chlorine-atoms with the walls of the vessel.
[3] Thon, *Z. physik. Chem.*, 124, 327, 1926.

in the same manner as X with chlorine atoms) the equation for the velocity becomes a combination of both given above.[2]

It seems therefore that the assumption of the atom-chain is very well proved. One may even go further. It is possible to estimate the absolute values of the constants k_2 to k_5. For this purpose we use in addition to the velocity measurements made with hydrogen and chlorine, those dealing with the combination of hydrogen and bromine and the observations of Weigert and Kellermann[4] from which the period of a chain may be estimated.

The following relationships, then, exist :—

(1) The yield of collisions (the fraction which gives rise to reaction) given by the reaction (3) $H + Cl_2 = HCl + Cl$ is twenty times that of reaction (4) $H + O_2 = \ldots$ (as stated by Cremer[5]) taking equal concentrations of Cl_2 and O_2. That means $k_4 : k_3 \sim 10^{-1}$.

(2) Oxygen does not appreciably check the combination of hydrogen and bromine ;[6] in other words, the reaction $H + O_2$ is much slower than $H + Br_2$.

(3) The reaction $H + Br_2 = HBr + Br$ occurs with every collision or with every tenth one. This follows, with a very great degree of probability, from the hydrogen-bromine-measurements; it will be made sure by what follows.

Therefore the yield of the collisions in the case of $H + O_2$ is—in gases at atmospheric pressure—of the order of 10^{-3}, and that for $H + Cl_2$ about 10^{-2}.

(4) The constant of the reaction $Cl + H_2$ is negligible[2] when compared with that of $H + Cl_2$. If we put it as one hundred times smaller the yield for that reaction becomes 10^{-4}.

(5) The same order of magnitude, or a still smaller one, must be ascribed[2] to the reaction $H + HCl = H_2 + Cl$.

(6) Finally, the k_5 of the reaction $Cl + O_2 = \ldots$ may be derived from the observation of Thon[3] that $\dfrac{k_3 \cdot k_4}{k_2 \cdot k_5} = \dfrac{1}{10}$. Thus, the yield of collisions in this reaction is 10^{-6}.

In this way the following orders of magnitude are ascertained for the yield of collisions for the different reactions :—

$H + Br_2$	$H + Cl_2$	$H + O_2$	$Cl + H_2$	$H + HCl$	$Cl + O_2$
10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-4}	10^{-6}
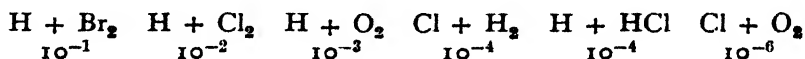
In these calculations every reaction which is not appreciable in comparison with another one is assumed to be only a hundred times slower than the other. One could assume these differences to be greater. But that cannot be done; it would produce an inconsistency with the time needed for the whole period of a chain, according to Weigert and Kellermann, and for the same reason $H + Br_2$ cannot have a smaller yield than 10^{-1}. Weigert and Kellermann illuminated a chlorine-hydrogen-mixture with a spark of 10^{-6} seconds; they observed a streak produced by the heat of the reaction growing stronger and stronger during 10^{-2} second and disappearing again within a tenth of a second.

Trifonoff[7] has already made the following calculations from these

[4] Weigert and Kellermann, Z. physik. Chem., 107, 1, 1923.
[5] Cremer, Ibid., 128, 285, 1927.
[6] Bodenstein and Lütkemeyer, Ibid., 114, 208, 1925.
[7] Trifonoft, Ibid., B3, 195, 1929.

observations for the yield of collisions: within 10^{-2} seconds the atoms forming the chain have something of the order of 10^{10}. $10^{-2} = 10^8$ collisions with molecules at pressures of one atmosphere. If one assumes the length of the chain—the yield for one quantum—according to an estimate by Göhring,[8] being 10^5 then it follows that only every thousandth collision is successful, whereas, of course, the question remains open whether $H + Cl_2$ or $Cl + H_2$ has this small yield.

The slower of the two must, therefore, have a yield of 10^{-3}. The calculations given above claim 10^{-4} for $Cl + H_2$. I think this figure agrees better with the chain period derived from the observation of the Schliere; the yield of 10^5 molecules per quantum as estimated by Göhring is too high. It may be reached with especially careful precautions, as we now know from direct determinations. But these precautions are not used in Weigert and Kellermann's experiments. Thus we may assume here a quantum-yield of 10^4, which leads to the value of the collision-yield 10^{-4} for $Cl + H_2$ given above.[9]

A certain number of other observations agree very well with the values of the different constants given above. I shall not give an account of them. Whilst the assumption of the atom chain gives an excellent interpretation of a great number of facts and even allows a quantitative estimation of the constants of their single reactions, there are other facts which cannot be explained by this assumption. The most important is that a very small content of water vapour is necessary to ensure the combination of hydrogen and chlorine. There is no longer any doubt that this is so, since Coehn and his co-workers[10] have determined the critical limits of the steam concentration, viz., that above which reaction takes place, and that below which it does not. Another fact of this kind, recently communicated by Allmand,[11] is that the quantum yield diminishes remarkably if one changes from visible light to ultra-violet. A similar change—in the opposite sense—holds for the formation of water. Weigert has succeeded in changing 40 per cent. of hydrogen into water by illuminating a mixture of 50 per cent. hydrogen, 25 per cent. oxygen, 25 per cent. chlorine with a quartz-mercury lamp,[12] whilst in visible light, Cremer[5] found that with equal concentrations of chlorine and oxygen the relation between hydrogen chloride and water was 20 : 1.

It is impossible to understand these facts from the standpoint of the atom-chain. But there are other phenomena still which, at least, present considerable difficulty. Firstly, the action of inhibitors which, even present in the smallest concentrations, prevent any combination of chlorine and hydrogen, thus producing the induction period which has given so much trouble to earlier investigators. On the other hand a more precise discussion of reaction (4) and (5) between hydrogen or chlorine atoms and oxygen, finishing the chain, leads to results which cannot, at any rate, readily be connected with the simple atom chain.

We have treated these reactions as normally bimolecular, without regard to the question whether that view is correct, and have obtained an excellent

[8] Göhring, Z. Elektroch., 24, 235, 1918.

[9] Jshikawa, Z. physik. Chem., B10, 299, 1930—has communicated new experiments, similar to those of Weigert and Kellermann, from which the period of a chain seems to be a little longer—this agrees with what is said above. But these experiments are not incontrovertible. Especially it is not sure if the membrane used has been free from hysteresis. If so the method could become very useful.

[10] Coehn and Tramm, Z. physik. Chem., 105, 356, 1923; Coehn and Jung, Z. physik. Chem., 110, 705, 1927.

[11] Allmand, J. Chem. Soc., 2709, 1309.　　[12] Weigert Ann. Physik., 24, 243, 1907.

agreement between the calculated velocity law and the observation. This kind of calculation would be allowable, if the reactions were

$$H + O_2 = OH + O \quad \text{and} \quad Cl + O_2 = ClO + O$$
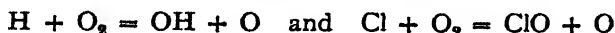
but both these changes are endothermic and do not occur at room temperature.

Thus one could write

$$H + O_2 = HO_2 \qquad Cl + O_2 = ClO_2$$

Neither HO_2 nor ClO_2 are to be found within the illuminated chlorine hydrogen mixture,[13] but that would not be a serious objection since they could disappear again in very rapid reactions. But the formation of both these substances ought to need a three body collision for their stabilisation. Therefore the breaking of the chains ought to increase with the pressure and we may ask whether such an influence of pressure can be found in the experiments.

The greatest number and the most exact of the experiments are those of Thon.[8] He did not appreciably vary the general pressure but he varied over a wide range the relations $[H_2] : [Cl_2] : [HCl]$. His results are excellently reproduced by the atomchain, with bimolecular reactions $H + O_2$, $Cl + O_2$. Thus the influence of the concentration of those three reactants, upon the stabilisation of HO_2 or ClO_2 must have been the same, an assumption which is certainly not unwarranted.[14]

Just as in Thon's investigations, in most other experimental researches there are no such great changes of the pressure as would serve to answer the question whether it really has an influence. But there are two special researches made with really widely changed pressure. Trifonoff[14a] studied the influence of the walls, comparing the velocity in a narrow vessel with that in a wider one. In this reaction, the action of the walls being not very marked, the reaction was directly proportional to the pressure under the influence of the same intensity of the illumination. With the small pressures used in these experiments, $[Cl_2] \sim [H_2]$ varying from 2·3 to 23 mm. Hg, the amount absorbed is proportional to the concentration

[13] HO_2 has up to the present only been found, by the mass-spectrograph method, in a mixture of hydrocarbons and oxygen, according a kind personal communication of Dr. Eisenhuth-Oppau, who gives an account on similar observations in *Z. Elektrochemie*, **36**, 654, 1930. Unsuccessful attempts to find ClO_2 in an illuminated mixture of chlorine and oxygen has been made by Frl. Kornfeld (method : changing of pressure) and by Dr. Schumacher (most sensitive method : absorption bands of ClO_2). Both private communications.

[14] One could directly write those reactions as really termolecular. Then all are exo thermic and may run with nearly the same constants :

$$H + O_2 + H_2 = H_2O + OH + 100 \text{ Cal.}$$
$$H + O_2 + Cl_2 = HCl + ClO_2 + 51 \text{ Cal.}$$
$$H + O_2 + HCl = H_2O + ClO + 67 \text{ Cal. or more}$$
$$Cl + O_2 + H_2 = H_2O + ClO + 60 \text{ Cal. or more}$$
$$Cl + O_2 + Cl_2 = Cl_2O + ClO + 4 \text{ Cal. or more}$$
$$Cl + O_2 + HCl = HClO + ClO + 11 \text{ Cal or more}$$
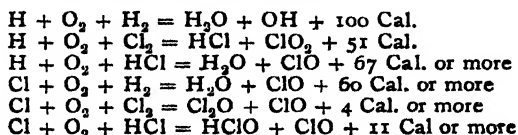
Here the heat of formation of ClO is taken from Wagner, *Z. physik. Chem.*, **B 5**, 199, 1929, and Bodenstein and Schumacher, *Z. physik. Chem.*, **B 5**, 227, 1929. The heat of solution of HClO is taken as 5000 cal. It is, of course, not claimed that these equations may be valid in detail. They only serve to show that such termolecular reactions are possible.

[14a] There is another investigation by Trifonoff (*Z. physik. Chem.*, **B 6**, 118, 1929), and others by Marshall, (*ibid.*, **29**, 1453, 1925), and Rollefson (*J.A.C.S.*, **51**, 770, 1929), using extremely low pressure. In this case also the wall-action is also important in the discoveries of the homogenous gas-phase reaction.

of chlorine. The same result was found in 1913 by Bodenstein and Dux,[15] as distinguished from the fact that during a single experiment the velocity was proportional to the square of $[Cl_2]$ or to $I_{abs.} . [Cl_2]$. This discrepancy was easily resolved, the velocity was given by

$$\frac{d[HCl]}{dt} = k . \frac{I_{abs.} . [Cl_2]}{[O_2]},$$

and since the chlorine was always accompanied by a small but nearly constant contamination of oxygen, an increase of $[Cl_2]$ in the numerator was always accompanied by the same increase of $[O_2]$ in the denominator.

We may assume that the same thing happened in Trifonoff's experiments, in which case the influence of pressure which we ought to expect would not be found. This conclusion, of course, though probable is somewhat uncertain. The same applies to another investigation made by Bogdandy and Polanyi,[16] who inaugurated the combination of hydrogen and chlorine not by light, but producing the chlorine atoms by the reaction

$$Na + Cl_2 = NaCl + Cl.$$
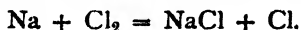
The pressure of their chlorine-hydrogen mixture was 10 mm. Hg or less— that of Na being very small—and the number of molecules of HCl for one primary Cl, was in some cases 10^4, not less than with atmospheric pressure when no special precautions were taken against small contaminations.

Both these investigations though they do not prove directly that the pressure has no influence make it probable. Now, if the atom chain is finished by termolecular reactions, and that must be so, this influence ought to exist: the higher the pressure, the smaller the yield. That it does *not* exist is an objection against the atom chain, although the investigations cited do not yet point so definitely in this direction that this conclusion can be accepted without doubt.

Doubtless the fact that perfectly dry "Chlorknallgas" does not react is a serious objective. This question has recently been treated, in connection with general considerations about the heats of activations in bimolecular reactions, by Franck and Rabinowitsch.[17] These authors, from special assumptions as to the structure of molecules are led to the conclusion that the reactions forming the atom chain ought to involve a large heat of activation and could not take place at room temperature. This is in agreement with the fact that the chlorine atoms produced by the absorption of light by the chlorine molecule do not react with hydrogen in the absence of steam. Thus, as the authors suggest, if steam is present, instead of $Cl + H_2 = HCl + Cl$, other reactions occur, for instance

(I) $\quad Cl + H_2O = ClH_2O, \quad ClH_2O + H_2 = H_2O + HCl + H,$

or $\qquad$ (II) $\quad Cl + H_2O + H_2 = HCl + H_2O + H.$
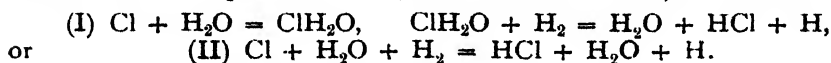
Such an intermediate action of steam does not formally preclude the atom chain. There is no difficulty in extending their scheme with respect to these reactions. If we use reactions such as (I) we may write (considering, for the sake of simplicity only, the end as $H + O_2$).

(1) $\quad Cl_2 + E = 2Cl$

(2) $\quad Cl + H_2O = ClH_2O$

(2') $\quad ClH_2O + H_2 = HCl + H + H_2O$

(3) $\quad H + Cl_2 = HCl + Cl$

(4) $\quad H + O_2 = \ldots$

[15] Bodenstein and Dux, *Z. physik. Chem.*, 85, 297, 1913.
[16] Bogdandy and Polanyi, *Z Elektrochem.*, 33, 554, 1927.
[17] Franck and Rabinowitsch, *Ibid.*, 36, 794, 1930.

Then we have for the stationary state :

(I) $\dfrac{d[\text{Cl}]}{dt} = 2I - k_2 \cdot [\text{Cl}] \cdot [\text{H}_2\text{O}] + k_3 \cdot [\text{H}] \cdot [\text{Cl}_2] = 0.$

(II) $\dfrac{d[\text{H}]}{dt} = k_2' \cdot [\text{ClH}_2\text{O}] \cdot [\text{H}_2] - k_3 \cdot [\text{H}] \cdot [\text{Cl}_2] - k_4 \cdot [\text{H}] \cdot [\text{O}_2] = 0.$

(III) $\dfrac{d[\text{ClH}_2\text{O}]}{dt} = k_2 \cdot [\text{Cl}] \cdot [\text{H}_2\text{O}] - k_2' \cdot [\text{ClH}_2\text{O}] \cdot [\text{H}_2] = 0.$

(I + II + III) $2I - k_4 \cdot [\text{H}] \cdot [\text{O}_2] = 0. \qquad [\text{H}] = \dfrac{2I}{k_4[\text{O}_2]},$

(I + III) $2I + k_3[\text{H}] \cdot [\text{Cl}_2] = k_2' \cdot [\text{ClH}_2\text{O}] \cdot [\text{H}_2].$

Here $2I \ll k_3 \cdot [\text{H}] \cdot [\text{Cl}_2]$ (long chain), and it follows, therefore, that for the formation of HCl

$$\dfrac{d[\text{HCl}]}{dt} = k_2' \cdot [\text{ClH}_2\text{O}] \cdot [\text{H}_2] + k_3 \cdot [\text{H}] \cdot [\text{Cl}_2] = \dfrac{4k_3 \cdot I \cdot [\text{Cl}_2]}{k_4 \cdot [\text{O}_2]}.$$

This is the same equation as that derived from the simple atom chain, which agrees with the experiments so long as $[\text{H}_2]$ is not smaller than $[\text{Cl}_2]$ and may easily be changed, if necessary, by considering the reaction $\text{Cl} + \text{O}_2$. Steam has no influence on the equation, because in these chain reactions the intermediate products are again formed as they are consumed and as a result steam *per se* is not consumed.

But this can hold good only so long as the condition of our type of calculation is fulfilled, *i.e.*, so long as it is permissible to consider a stationary state in which especially

$$\dfrac{d[\text{ClH}_2\text{O}]}{dt} = k_2 \cdot [\text{Cl}] \cdot [\text{H}_2\text{O}] - k_2' \cdot [\text{ClH}_2\text{O}] \cdot [\text{H}_2],$$

may be put equal zero ; or, in other words, so long as the consumption of ClH_2O is equal its regeneration by Cl and H_2O. This will no longer happen if the concentration of H_2O becomes smaller than some critical value, in which case the reaction velocity decreases and finally becomes zero, whilst above this value steam concentration has no influence.

Thus, this interpretation of steam catalysis is in full qualitative agreement with the facts. But if one makes a quantitative calculation the greatest difficulties arise. Coehn and Jung [10] have found that this critical concentration of steam, at which the reaction velocity decreases rapidly, is equal to 10^{-5} or 10^{-4} mm., $\text{Hg} = 10^{-9}$ mols./l. On the other hand, the reaction velocity in the experiment with this concentration was $0 \cdot 1$ millimol HCl in 9 c.c. and in 6 minutes $= 3 \times 10^{-5}$ mols./l. sec. This velocity is due in equal parts to the reactions (2′) and (3), and therefore $k_2' \cdot [\text{ClH}_2\text{O}] \cdot [\text{H}_2]$ must be 10^{-5} mols./l. sec. That is possible, as may easily be estimated ; but it is also necessary that ClH_2O be rebuilt with the same speed by reaction (2), and that is impossible. The maximum value of k_2 is 10^{11}—the number of collisions for a bimolecular reaction if we neglect the fact that for the stabilisation of ClH_2O a three-body collision is needed. This makes it necessary, for reaching $k_2 [\text{Cl}] \cdot [\text{H}_2\text{O}] = 10^{-5}$ mols./l. sec., that, taking $[\text{H}_2\text{O}] = 10^{-9}$, $[\text{Cl}]$ must be not less than 10^{-7}. Such a high concentration of Cl atoms is, however, impossible. As one may conclude by analogy from the behaviour of bromine atoms, and as we have directly stated by studying the formation of phosgene and the photosensitised contemporary forma-

tion of carbon dioxide,[18] the chlorine atoms begin to recombine in the gas phase and to diffuse to the walls of the vessel, if their concentration is 10^{-10} mols./l. It is impossible therefore that the concentration of the [Cl] in the $H_2 + Cl_2$ reaction should become higher than 10^{-10} mols./l. Even with the (doubtless too high) value of 10^{11} for k_2 a sufficiently rapid formation of $Cl . H_2O$ is impossible. The steam catalysis cannot be understood by this way.

The same holds true for a second possibility mentioned by Franck and Rabinowitsch, a three-body reaction

$$Cl + HOH + HH = ClH + OHH + H.$$

Qualitatively, again, we are led to the same result as by the old atom chain, this termolecular reaction replacing the old reaction (2). But a quantitative calculation demands that with $[H_2O] = 10^{-9}$, $[Cl] = 10^{-10}$ the termolecular constant k_2 must be 10^{16} whilst it cannot be greater than 10^9.

Finally, the assumption of an additional compound H_2H_2O instead of ClH_2O gives the same difficulties as that last mentioned, and we must conclude, therefore, that within the assumption of the atom chain it is impossible to explain steam catalysis by such intermediate reactions with water.

Now let us assume that no real additional compounds are formed with water, but that there is an energy transfer from the water molecules to those of Cl, or of H_2, or to both at the moment of the collision. We know that such energy transfer may occur at a much greater distance than that of a real collision, as calculated from the kinetic theory, especially if there is a good resonance between sender and receiver, as derived from the wave mechanics by Kallmann and London.[19]

Here, again, we find that our old velocity equations result; it is, however, impossible that this activation can occur sufficiently rapidly. I shall not give again in detail this calculation. Although at first I had hoped this would lead to a satisfactory conclusion, such is really far from being possible. The final conclusion is that, within the assumption of the atom chain, it is impossible to explain the catalysis by traces of steam, either by intermediate chemical reactions or by an energy transfer.

The above-mentioned paper of Franck and Rabinowitsch was first read before a meeting of the *Bunsengesellschaft* in May, 1930, and then published in the *Z. Elektrochemie* in September, 1930. Just before Christmas our Göttingen colleagues had invited us to a small symposion on such questions. Here I learned during the discussion with Professor Franck that this paper had not the significance which I (and I think other readers too) understood, *viz.*, that the action of water ought to occur at every step of the atomic chain, but, rather, that this should occur only at the first step. In this case the steam molecule acts only as a catalyst in the formation of a hydrogen atom and, in the further course of the chain there no chlorine atoms enter. This means that the old atom chain must be replaced by another one, for which Professor Franck suggested, without closer discussion, something like

$$H + H_2 + Cl_2 = 2HCl + H.$$
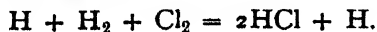
The rôle of the steam molecules in this first step is to prevent the chlorine atoms, which cannot react with hydrogen molecules, reaching the walls to

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[18] Shortly to be published.
[19] Kallmann and London, *Z. physik. Chem.*, B **11**, 100, 1930.

be recombined there, thus failing to initiate chains, as they would do if enough steam were present.

If we assume such a chain to be possible this interpretation of Franck and Rabinowitsch is very reasonable.   The first steps of the reaction would be

$$(1)\ Cl_2 + E = 2Cl$$
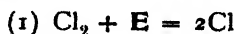
$$(2)\ Cl + H_2O + M = ClH_2O + M \text{ followed by } ClH_2O + H_2 = HCl + H_2O + H$$

or instead of both these reactions: $Cl + H_2O + H_2 = HCl + H_2O + H$, and then any chain in which no more chlorine atoms appear.   With the reactions (2) there would be, in competition,

$$(2')\ Cl \rightarrow wall = \tfrac{1}{2}Cl_2$$

The distribution of the Cl atoms between the reactions (2) and (2') would be $k_2 . [H_2O] . [M] : k_2'$.   Here k_2 is the termolecular collision number, 10^9 if the concentrations are given in mols., whereas k_2' is the fraction of chlorine atoms reaching the walls within one second.   This figure is, as estimated from known diffusion constants, and as we have proved, calculating the formation of phosgene a little higher than unity for normal sized vessels and for gases at atmospheric pressure.

The number of beginning chains, then, becomes

$$2I . \frac{k_2 . [H_2O] . [M]}{k_2' + k_2 . [H_2O] . [M]} = 2I . \frac{[H_2O] . [M]}{10^{-9} + [H_2O] . [M]}.$$

The critical concentration of steam as given by Coehn and Jung is 10^{-9} mols./l. With this concentration one hundredth of all chlorine atoms would give rise to a chain.   Again, 10^{-6} mols. ($= 0.02$ mm.) steam would be sufficient to allow 90 per cent. of all the chlorine atoms to start a chain, whilst with 10^{-11} mols. ($= 2 \times 10^{-7}$ mm.) only 10^{-4} of the atoms would do so.   This is, at least approximately, what is given by the experiments.

Now let us seek a series of reactions which may give a chain which, without chlorine atoms, leads to the observed velocity laws.   At first sight this seemed to be impossible and my younger collaborators [20] and myself were led to reject all attempts, because the new initiation of the chains ought to be a termolecular reaction, whilst we were accustomed to treat the chain-breaking reactions $H + O_2$ and $Cl + O_2$ as bimolecular, thus getting an accelerating influence of the pressure on velocity.

But since it is necessary to write those reactions also as termolecular (see page 416) this difficulty disappears, and we can construct more than one series of reactions which fulfils our demands.   One of these is that which uses the chain suggested by Franck at the Göttingen symposion
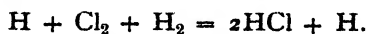
$$H + Cl_2 + H_2 = 2HCl + H.$$

If we combine this with suitable reactions breaking the chain we have

$$(1)\ Cl_2 + E = 2Cl.$$
$$(2)\ Cl + H_2O + H_2 = HCl + H_2O + H.$$
$$(3)\ H + Cl_2 + H_2 = 2HCl + H.$$
$$(4)\ H + O_2 + H_2 = H_2O + OH.$$
$$(5)\ H + O_2 + Cl_2 = HCl + ClO_2.$$

[20] One of whom, Dr. Bernreuther, is occupied with an experimental research on the " dry " reaction and is thus extremely interested in this question.

Here we suppose first that there is enough H_2O to allow all chlorine atoms to react according to (2) and we further assume that reactions (4) and (5) are followed each by one single reaction namely

(4') OH + H + M = H_2O + M, and
(5') ClO_2 + H = HCl + O_2.
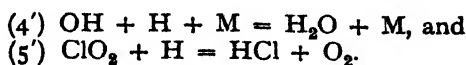
With both these assumptions we have for the stationary state

$$\frac{d[H]}{dt} = 2I - 2k_4 \cdot [H] \cdot [O_2] \cdot [H_2] - 2k_5 \cdot [H] \cdot [O_2] \cdot [Cl_2] = 0,$$

$$[H] = \frac{I}{[O_2] \cdot (k_4 \cdot [H_2] + k_5 \cdot [Cl_2])}.$$

From which we deduce,

$$\frac{d[HCl]}{dt} = 2k_3 \cdot [H] \cdot [Cl_2] \cdot [H_2] = \frac{2k_3 \cdot I \cdot [Cl_2] \cdot [H_2]}{[O_2] \cdot (k_4 \cdot [H_2] + k_5 \cdot [Cl_2])}.$$

Thus, in the simplest manner we have arrived at the equation verified by Thon in the most careful experiments.

If in oxygen-free gases a reaction with a chloride of silicon or a similar substance breaks the chains this cannot be done by a reaction such as

H + X = Y   or   Y + HCl,
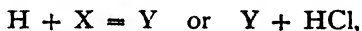
but it must happen by some such reaction as

(6) H + Cl_2 + X = HCl + Y + Cl_2.
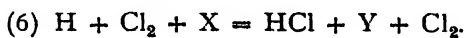
This gives the observed result

$$\frac{d[HCl]}{dt} = \frac{4k_3 \cdot I \cdot [H_2]}{k_6 \cdot [X]},$$

whilst with the first reaction there remains a $[Cl_2]$ in the numerator, and this does not correspond with the facts.

It may be that this special question will be resolved better by another method; it may be also that the suggested mechanism may be better replaced by a similar one—though I doubt it, because it is the simplest one and generally the simplest is the best. I will not discuss these problems in detail, firstly, because I have not yet had the time for the necessary calculations and, secondly, because such a discussion ought to be accompanied by experimental research. What I have sought to show is merely that it certainly is possible to find a chain mechanism which uses chlorine atoms only for starting the chains, thus enabling us on the one hand to understand the rôle of steam in the manner suggested by Franck and Rabinowitsch and that this mechanism agrees also with the observed velocity laws.

This separation of the intermediate substances into chlorine atoms which start the chains, and others which continue them, makes understandable three phenomena which have not as yet been thoroughly discussed. Firstly, the enormous action of NH_3, NOCl, Cl_2O, ClO_2, O_3 and all such substances which (as accidental contaminations or intentional additions) completely inhibit the reaction until they are fully used up. All these substances react on almost every collision with chlorine atoms; possibly with hydrogen atoms too, but this is unimportant for the present. If they come

nto competition in the atom chain with the reaction $Cl + H_2 = HCl + H$ they may of course have an inhibitory influence. But they are in competition with a substance of high concentration and if their own concentration becomes small the inhibitory effect must do the same. In the new chain the competition is between the reaction

(1) $Cl + H_2O + H_2 = HCl + H_2O + H$ and, for instance,

(2) $Cl + O_3 = ClO + O_2$.
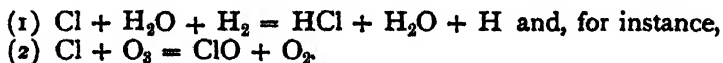
The first reaction is termolecular, one of the reactants, H_2O, being present in very small concentrations. The second is bimolecular, and occurs a thousand times more frequently even if the concentration of O_3 is not higher than that of H_2O. The enormous effect of these substances may easily be understood by this comparison.

Both the other facts which may be elucidated by the assumption that no more chlorine atoms appear within the run of the chains are concerned with the variation in the yield on changing from visible light to ultraviolet. Here recently Allmand[1] has made the most surprising observation that the yield decreases remarkably with shorter wavelengths (the yield of course for one quantum absorbed) and, on the other hand, there is the old research of Weigert,[12] who succeeded in converting 40 per cent. of the hydrogen into water by illuminating a mixture of 50 per cent. H_2, 25 per cent. O_2, 25 per cent. Cl_2 with a quartz-mercury lamp, whilst in visible light Cremer[5] stated that with equal concentrations of Cl_2 and O_2 the yield of HCl was twenty fold that of H_2O.

As long as chlorine atoms act as chain links it cannot make any difference whether the primary atoms are produced by longer or by shorter waves because the primary atoms are only a very small fraction of the whole. But if there are, exclusively, primary chlorine atoms, then it makes a great difference whether they are produced with a small excess of energy by visible light or by ultra-violet with a great excess which they store up as kinetic energy.

In competition with the starting reaction of the new series

(2) $Cl + H_2O + H_2 = HCl + H_2O + H$
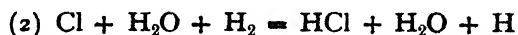
there will now be a reaction

(2′) $Cl + O_2 + H_2 = H_2O + ClO$.

If this has some heat of activation it will not be noticeable in visible light, but there may be a competition for (2) if chlorine atoms bring with them a high energy. The difference between the energy of 4500 and 3000 Å. is sufficiently large to lead to this competition, even though it be granted that this primary energy is partly dissipated by collisions.

Thus the observations of Allmand, Weigert and Cremer are connected together and may be understood by a deduction which necessarily must be drawn from the assumption that chlorine atoms only act as initiators of the chain and no longer as their links.

Finally let us consider whether the time which has been found by Weigert and Kellermann to be necessary for a single chain agrees with this new mechanism.

Here two processes need time: the start of the chain and its run, the reaction

$$Cl + H_2O + H_2 = HCl + H_2O + Cl$$
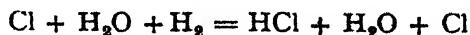
which occurs only once, and

$$H + H_2 + Cl_2 = 2HCl + H$$
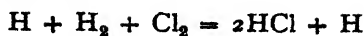
which is repeated some 10^4 times.

For the latter reaction we may assume that every three-body collision is successful. Then the hydrogen atom has with chlorine and hydrogen molecules (each of half an atmosphere)

$$10^{10} \times \tfrac{1}{2} \times \tfrac{1}{2} \times 10^{-3} = 2 \cdot 5 \times 10^6$$

collisions per second or one collision each 4×10^{-7} seconds, those 10^4 collisions giving the yield per one quantum within 4×10^{-3} seconds. This time, of course, would be longer if only a fraction of all the collisions is followed by reaction. On the other hand the chlorine atom starting the chain has

$$10^{10} \times [H_2] \times [H_2O] \times 10^{-6}$$

three body collisions per second with molecules of H_2 and H_2O, where the concentrations are given in atmospheres, or an average time for such a collision of $\dfrac{10^{-7}}{[H_2] \cdot [H_2O]}$ seconds. If we suppose $[H_2O] = 10^{-3}$ mm. $= 10^{-6}$ atm., the smallest value above which an increase of the steam concentration no longer produces any rise of the reaction velocity exceeding the average time needed for starting a chain (with $[H_2] = \tfrac{1}{2}$ atm.) is $0 \cdot 2$ second. If the steam concentration is twenty times higher this time would be 10^{-2} second as observed by Weigert and Kellermann. This concentration being perfectly reasonable for those experiments, there is a good agreement.

This time must vary appreciably with the steam concentration. Its highest value would be something like a second, since with smaller steam concentrations the chlorine atoms—with normal gas pressures and "normal" sized vessels—are recombined on the walls instead of producing chains. The smallest value, on the other hand, would be that needed by the run of the chain, for a yield of 10^4 mols. per Einstein at least $4 \cdot 10^{-3}$ seconds as shown above. We should obtain much enlightenment on the subject ·by proving these conclusions experimentally.

After all, this new conception of the chlorine hydrogen chains, based on the suggestion of Franck and Rabinowitsch, is for many reasons superior to the old atom chain. There are many opportunities still for examining it by new experiments,[21] but it may be expected that it will stand such proof.

I have no more I wish to say concerning the chlorine-hydrogen reaction. I would, however, add a remark about the idea by which Franck and Rabinowitsch have been led to this treatment of our reaction. This was the assumption that (in consequence of the structure of the molecules H_2, Cl_2 and the like) such a reaction as $Cl + H_2 = HCl + Cl$ needs a large energy of activation for separating both the nuclei of the molecule — and cannot therefore occur at room temperature. The "Chlorknallgas" observations are in best agreement with this conception. Neither $Cl + H_2 = HCl + Cl$, nor even $H + Cl_2 = HCl + Cl$ which is exothermic with 44 Cal. per mol., is found to occur. The reaction $H + Cl_2 + H_2 = 2HCl + H$ may at first sight be regarded as of the

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[21] The most striking seems to be that the critical value of the steam concentration must vary distinctly with the pressure. The reaction $Cl + H_2O + H_2$ must grow quicker with increase of pressure, the diffusion to the walls slower.

same nature, thus disapproving what ought to be proved; but in this three-body collision the influence of the different atoms may easily be given by a conception such as

$$H + Cl—Cl + H—H = HCl + ClH + H$$
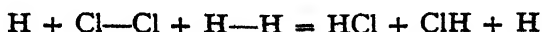
in order to make it clear that, under the influence of the neighbouring atoms, 2HCl may be formed without producing, even for short time, a free chlorine atom.

So far this seems to be all right. But the same ought to be valid, for the molecules Br_2 and I_2 and also for a reaction $Br + H_2 = HBr + H$. In this case the hydrogen molecule, which cannot be split by the chlorine atom, reacts at every collision which is accompanied with an energy sufficient to cover the heat of this endothermic reaction. This has been shown especially by Herzfeld,[22] and the only question not yet clearly resolved is whether there is a very small heat of activation (1600 cal.) which can only reduce the yield of the collisions to a tenth at room temperature and which is without any interest for our discussion.

It is true that the measurements with bromine and hydrogen are not made with extremely dry gases, but there is no time for a three-body inter-action of steam present in small concentrations, as in the case of hydrogen chloride formation, since every bimolecular collision which fulfils the above-mentioned energy conditions leads to reaction.

The same objection may be derived from the reactions $H + Br_2 = HBr + Br$ and $H + HBr = H_2 + Br$ as may easily be derived from the bromine-hydrogen which occur at nearly every collision, and the same seems, at least, to be true for the reaction $H + HI = H_2 + I$ as may be concluded from Warburg's research into the photochemical decomposition of hydrogen iodide. For this reason, the basis of the reasoning of Franck and Rabino-witsch, although its application to the chlorine hydrogen reaction is very successful, seems to be not yet beyond doubt.

[22] Herzfeld, *Ann. Physik.*, **59**, 635, 1919.

GENERAL DISCUSSION.

On Part II., Papers 1 and 1a.

Dr. R. O. Griffith (*Liverpool*) said : One or two objections to the interesting mechanism suggested by Professor Bodenstein for the photo-combination of hydrogen and chlorine may be advanced. These relate to the postulated reactions (4), (4'), (5), and (5'), the reactions which terminate the chain. In these the formation of ClO_2 is suggested (process (5)), together with its further reaction with H atoms only. Yet ClO_2 acts as a strong inhibitor to the photo-combination, which action is interpreted by Professor Bodenstein by postulating that every—or nearly every—collision between ClO_2 and Cl destroys a Cl atom. The assumption that ClO_2 exists as an intermediary body must therefore entail—on the basis of this mechanism—a much larger retarding effect than that which Professor Bodenstein takes into account. Further, it does not seem allowable to postulate that the presumably active radicle OH formed in process (4) reacts only by way of (4'). A reaction

$$Cl—Cl + H—H + OH \rightarrow Cl + H—Cl + H—OH$$

would, by analogy with reaction (3)

$$H + Cl—Cl + H—H \rightarrow H—Cl + Cl—H + H$$

(the chain process of Professor Bodenstein's mechanism), appear to be a more likely process.

Finally, while the postulation of reactions involving three-body collisions doubtless enables some difficulties to be evaded, it is by no means a simplification of the problem. An adequate discussion of a mechanism of this type would require consideration of the possible results of all ternary collisions between the reacting entities H_2, Cl_2, HCl, H_2O, H, Cl, OH and ClO_2, and these possibilities are not few in number.

Professor M. Bodenstein (*Berlin*) (*communicated*) said : Dr. Griffith does not accept my assumption of a chain breaking reaction

$$H + O_2 + Cl_2 = HCl + ClO_2,$$
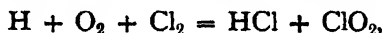
because ClO_2 is one of the strongest inhibitors which will react with the Cl atoms starting the chains. But there is no inconsistency. If one assumes that this reaction is followed in every case by $ClO_2 + Cl = Cl_2 + O_2$ the resulting velocity equation is exactly the same as that given in my paper as derived from a subsequent reaction $ClO_2 + H = HCl + O_2$.

Professor R. Mecke (*Heidelberg*), said : I will only call attention to the interesting fact that the dissociation energies of the HCl and H_2 molecules are exactly the same (101 cal./mol.). It might be possible therefore that in the energy exchange of the chain reaction some resonance phenomena will take place. The energy set free by the formation of HCl from the atoms is just sufficient to dissociate the hydrogen molecule ; in other words the reaction $Cl + H_2 = HCl + H$ will proceed without any apparent heat of reaction.

Professor A. J. Allmand (*London*) said : I should like to raise several points on Professor Bodenstein's paper on the $H_2 - Cl_2$ reaction :—

(*a*) HCl is known not to retard the reaction. This fact seems difficult to reconcile with any mechanism involving free H atoms. For it would appear, from the figures given by Bodenstein, that the following collision efficiencies hold good

$$H + HCl \qquad 10^{-4}$$
$$H + O_2 + H_2 \qquad 1$$

the latter corresponding to the figure of 10^{-3} given for the two-fold collision $H + O_2$. If this is so, then, as [HCl] will normally soon become much greater than $[O_2]$ (in reaction systems free from liquid water), should not the absolute rate of removal of H atoms by HCl molecules exceed that of removal of H atoms by O_2 molecules, and hence HCl retardation become important ? If, as I think is the case, the value of $K = \frac{[Cl][H_2]}{[H][HCl]}$ has been calculated to be of the order of 10, and this figure is correct, then $k_{H + HCl} > k_{Cl + H_2}$, which would reinforce the above argument.

(*b*) From the thermochemical data contained in a footnote to Professor Bodenstein's paper, one calculates

$$Cl + H_2 \rightarrow H + HCl - 7 \text{ Cals.}$$

If this is correct, then $Cl + H_2 + H_2O \rightarrow H + HCl + H_2O$ must also be endothermic, in which case it does not seem justifiable to use 10^9, the termolecular collision number, for calculating the distribution of Cl atoms between (2) this reaction and (2') $Cl + wall \rightarrow \frac{1}{2}Cl_2$.

(c) The work of Mr. E. Beesley on the effect of wavelength on the quantum sensitivity of the $H_2 - Cl_2$ reaction quoted by Bodenstein has been repeated by J. B. Bateman, using spectrally dispersed instead of filtered light. The new results confirm the former ones in the most important respect, i.e., the rapid fall off in γ in the ultraviolet, but do not show the maximum previously found in the violet. Commencing at 436 $\mu\mu$, and passing to shorter wavelengths, the relative value of γ is practically unchanged at 405 $\mu\mu$, drops to about 0·8 at 365 $\mu\mu$ and to 0·3 at 310 $\mu\mu$, and below 300 $\mu\mu$ falls very rapidly. It has been confirmed that the reaction takes place in the light of the mercury green line (546 $\mu\mu$); both in this case and with 492 $\mu\mu$, the γ values relatively to those in other parts of the spectrum fluctuate in a very marked manner. This is probably connected with the occurrence of what must be quite a different type of activation from that conferred by shorter wavelength light.

(d) As an explanation of the results of Messrs. Beesley and Bateman, alternative to that suggested by Professor Bodenstein, the following are proposed as possible reactions which may follow the primary formation of Cl atoms :—

(ii) $Cl + H_2O$ [+ M] $\rightarrow$ Cl, H_2O [+ M]
(iii) $Cl + H_2O$ $\rightarrow$ $HCl + OH - 11$ Cals.
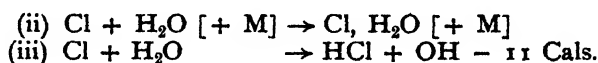
Process (iii), which is not followed by a chain (Frankenburger and Klinkhardt), would only take place if the Cl atom carried with it the necessary energy in the form of kinetic energy of translation. 11 Cals./gram atom means 22 Cals./mol. of chlorine, which, when added to the molecular heat of dissociation of Cl_2 to normal atoms (the important figure at atmospheric pressure) gives 79 Cals. This, in its turn, corresponds to 360 $\mu\mu$, which coincides sufficiently well with the wavelength at which the fall off in relative quantum efficiency begins.

In equation (ii), the third partner M of the threefold collision is bracketted in virtue of certain considerations communicated to the discussion on Part I. The experiments on which the above suggested mechanism is based were done in presence of a high water vapour pressure (Bunsen-Roscoe technique). In the course of work now being carried out, the effect of a reduction of this pressure on the $\gamma - \lambda$ function will be investigated. Such a reduction should presumably lead to a flattening out of the present curve.

(e) Mr. Bateman and I provisionally suggest a mechanism of the following type for the chain and for its termination, under normal conditions of $_{H_2O}$, p_{O_2}, total pressure and diameter of vessel :—

(iv) $Cl, H_2O + H_2 + M \rightarrow M + H_2Cl, H_2O$
(v) $H_2Cl, H_2O + Cl_2 \rightarrow 2HCl + Cl, H_2O$
(vi) $H_2Cl, H_2O + O_2 \rightarrow HCl + H_2O + HO_2$

and perhaps

(vii) $H_2Cl, H_2O + O_2 + H_2 \rightarrow HCl + 2H_2O + OH$
(viii) $H_2Cl, H_2O + O_2 + Cl_2 \rightarrow HCl + H_2O + HO_2 + Cl_2.$
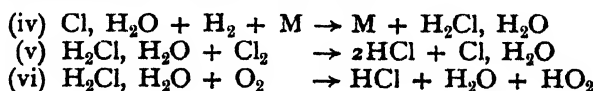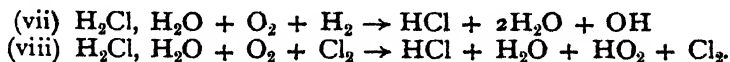
The HO_2 will pass through the stage of H_2O_2 (Norrish ; Frankenburger and Klinkhardt), and will finally yield O_2 and either H_2O or HCl.

It will be noticed that H atoms do not appear. H_2Cl is formally analogous to COCl, used by Bodenstein in the $COCl_2$ reaction mechanism. The existence of H_2Br has been assumed by Franck in another connection. Reaction (iv) is shown as a threefold collision, but the participation of M

may not be essential if the suggestion contributed to the discussion on Part I. is correct. If (vii) and (viii) are appreciable compared with (vi), the conditions will respectively correspond to or be similar to the hydrogen retardation alleged by Chapman.

Professor M. Bodenstein (*Berlin*) (*communicated*), in reply to Professor Allmand's remarks :—

With regard to points (*a*) and (*b*), the reaction $Cl + H_2 = H + HCl$ is thermo-neutral ($H_2 + Cl_2 = 2HCl + 44$ Cal., $Cl + Cl = Cl_2 + 57$ Cal., $H + H = H_2 + 101$ Cal.); I think, therefore, that a reaction $Cl + H_2 + H_2O = H + HCl + H_2O$ can occur at every (three-body) collision, and the equilibrium $\dfrac{[Cl][H_2]}{[H].[HCl]}$ may have a constant K of the order of unity.

From the fact that HCl does not retard the reaction there arises a result which is easily derived from the assumption of an atom chain, if the constant of $H + HCl = H_2 + Cl$ is put $\leq 10^{-4}$.

I no longer think, however, that the assumption of the old atom chain is justifiable.

With regard to points (*c*) and (*d*), I entirely agree that there may be a reaction such as (iii) which explains the decrease in the quantum efficiency. My own suggestion was entirely provisional, but I think that of Professor Allmand is also provisional. It will not be at all easy to elucidate this question completely.

With regard to point (*e*), a mechanism involving H_2Cl was one of those which, as mentioned in my paper, I had found suitable. That which was there discussed in detail was the most simple mechanism.

Dr. R. G. W. Norrish (*Cambridge*), said : I am hoping that some further data relevant to the mechanism proposed by Professor Bodenstein will be forthcoming about the hydrogen-chlorine reaction as a result of measurements of the relative quantum efficiency of formation of H_2O and H_2O_2 in the H_2—Cl_2—O_2 system which we have underway. For my part I do not feel that it is likely that ClO_2 enters into the reaction as suggested by Professor Bodenstein. Its removal by chlorine atoms as he suggests would necessarily be slow, and its concentration would rise to a degree which should render its detection possible. I believe that it has been looked for on more than one occasion, in particular, by Schumacher, and always with negative results. On the other hand, I have shown that the formation of H_2O_2 is clearly demonstrable, and I think it at present appears preferable to restrict the chain-ending mechanism to reaction between H atoms and oxygen molecules, and to exclude the formation of comparatively stable oxides of chlorine unless they can be detected.

Professor A. Berthoud (*Neuchâtel*), said : The variations of the velocity of this reaction as a function of the luminous intensity and of the concentrations of the chlorine, hydrogen, and oxygen, are very complex, and none of the formulæ, by which attempts have been made to express the reaction as a whole, really holds good for every concentration of the gases taking part in the phenomenon. The observed facts, then, can only be satisfactorily expressed by means of a number of formulæ each of which holds good in a limited sphere.

When the pressure of hydrogen is small relatively to that of chlorine the velocity of photosynthesis is expressed, in accordance with the measurements of Mrs. Chapman [1] by the equation :

$$d[ClH] : dt = k[Cl_2][H_2]^{\frac{1}{2}} . \qquad . \qquad . \qquad . \quad (1)$$

[1] M. C. C. Chapman, *J. Chem. Soc.*, **123**, 3062, 1923 ; see also A. Berthoud, *Helv. Chim. Acta*, **7**, 324, 1924.

These measurements indicate that the retarding influence of oxygen is not exhibited in these conditions; it takes place only when the pressure of the hydrogen exceeds a certain limit.

When the partial pressures of the hydrogen and of the chlorine are of the same order, the velocity of the reaction is given roughly by the formula:
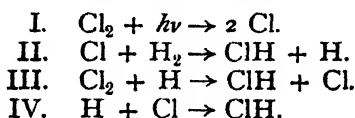
$$\frac{d[\text{Cl H}]}{dt} = kI_0 \frac{[\text{Cl}_2]^2}{[\text{O}_2]} \qquad . \qquad . \qquad . \qquad . \quad (2)$$

This relationship found by Bodenstein and Dux [2] is only approximate. Mrs. Chapman's measurements have shown that the velocity increases less rapidly than the square of the concentration of chlorine, and that, so long as the concentration of hydrogen is not too high, the velocity is expressed sufficiently closely by a relationship of the form:

$$\frac{d[\text{Cl H}]}{dt} = \frac{kI_0[\text{Cl}_2]^2[\text{H}_2]}{[\text{Cl}_2] + k'[\text{O}_2][\text{H}_2]} \qquad . \qquad . \qquad . \quad (3)$$

Nevertheless, this equation of itself provides only an approximation. The velocity increases a little less rapidly than the luminous intensity. Moreover, when the concentration of hydrogen is more and more increased, the velocity of the reaction is at first increased, as indicated by equation (3), but after having reached a maximum, it then decreases—a fact for which the formula does not account.

As a general rule, authors who have sought to explain the kinetics of the photosynthesis of hydrogen chloride have completely forgotten to take into account the fact that, when the pressure of hydrogen is small relatively to that of chlorine, the velocity is expressed by formula (1). The great importance of this arises from the fact that one may assume straight away that in this, as in other reactions of chlorine, the light· has the effect of dissociating the molecules of Cl_2, a fact which has sometimes been doubted. In order to explain formula (1) it is only necessary to assume the series of reactions represented by the following equations:—

I. $\quad \text{Cl}_2 + h\nu \rightarrow 2 \text{ Cl}.$
II. $\quad \text{Cl} + \text{H}_2 \rightarrow \text{ClH} + \text{H}.$
III. $\quad \text{Cl}_2 + \text{H} \rightarrow \text{ClH} + \text{Cl}.$
IV. $\quad \text{H} + \text{Cl} \rightarrow \text{ClH}.$

Calculation shows that, when the stationary condition is reached, the concentrations of atomic chlorine and hydrogen are given by the equations

$$[\text{Cl}] = \sqrt{\frac{k_1 \cdot k_3}{k_2 \cdot k_4}} \cdot I_0 \cdot \frac{[\text{Cl}_2]}{[\text{H}_2^{\frac{1}{2}}]} \qquad . \qquad . \qquad . \quad (4)$$

$$[\text{H}] = \sqrt{\frac{k_1 \cdot k_3}{k_3 \cdot k_4}} \cdot I_0^{\frac{1}{2}} [\text{H}_2]^{\frac{1}{2}} \qquad . \qquad . \qquad . \quad (5)$$

whilst for the velocity of formation of hydrogen chlorine we obtain:

$$\frac{d[\text{Cl H}]}{dt} = 2\sqrt{\frac{k_1 \cdot k_2 \cdot k_3}{k_4}} \cdot I_0^{\frac{1}{2}} \cdot [\text{Cl}_2][\text{H}_2]^{\frac{1}{2}} \qquad . \qquad . \quad (6)$$

We see that this equation, so far as concerns the influence of the concentrations of hydrogen and of chlorine is identical with equation (1)

which was found empirically. It is reasonable to assume, then, that in the case when the pressure of hydrogen is small in relation to that of chlorine, the velocity of the reaction is proportional to the square root of the luminous intensity; experimental figures on this point are, however, lacking.

We see, according to equations 4 and 5 that if we decrease the concentration of hydrogen while keeping that of chlorine constant, the product of the concentrations of atomic chlorine and hydrogen remains constant, and in consequence the same thing applies to the velocity of reaction IV. However, as the concentration of atomic chlorine goes on increasing we may imagine that if the pressure of hydrogen is sufficiently small, a new reaction ought to take place, namely :

$$V. \quad 2Cl \rightarrow Cl_2.$$
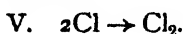
When reaction IV. becomes negligible, in comparison with V., the velocity is expressed by the equation :

$$\frac{d[ClH]}{dt} = 2k_2\sqrt{\frac{k_1}{k_2}} . I_0^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}[H_2] \qquad . \qquad . \qquad . \quad (7)$$

We might expect, then, that from the point of view of the hydrogen the order of the reaction would be likely to increase and to tend towards unity when the concentration of that gas becomes extremely small. This increase of the order in relation to the hydrogen has in fact been observed by Mrs Chapman. On the other hand Rollefson,[3] who has worked with a gaseous mixture under very low pressure in which the proportion of hydrogen was very small, has shown that in these conditions the velocity of the reaction is proportional to the concentration of the hydrogen.

If, on the other hand, we increase the proportion of hydrogen in the gaseous mixture, the concentration of atomic chlorine decreases and that of atomic hydrogen increases. Moreover, experience shows that in this case the retarding influence of oxygen commences to show itself and becomes more and more marked as the course of the reaction is little by little modified until it is given by formula 2.

We are forced by this to the conclusion that the retarding influence of oxygen does not arise, as we once assumed, from a reaction with atomic chlorine but from a reaction with atomic hydrogen. This is, moreover, the conclusion at which for other reasons Professor Bodenstein and Dr. Norrish have arrived. The velocity of this reaction ought to be proportional to the concentration of atomic hydrogen, for thus only can we explain the fact that the velocity of photosynthesis is simply proportional to the luminous intensity, if the proportion of hydrogen in the mixture is sufficiently great. In these conditions then we ought to assume, with Bodenstein and Norrish, the reaction :

$$VI. \quad H + O_2 \rightarrow H . O_2$$

succeeded in all probability by the following

$$VII. \quad H . O_2 + H_2 \rightarrow H_2O + OH.$$
$$VIII. \quad H + OH \rightarrow H_2O.$$
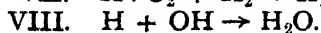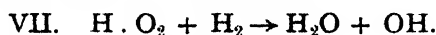
We may add that this point of view accords perfectly with the results of Cremer,[4] according to which each quantum of light absorbed gives rise to the formation of two molecules of water.

[3] J. Rollefson, *J. Am. Chem. Soc.*, **51**, 804, 1929.
[4] Cremer, *Z. physik. Chem.*, **128**, 285, 1927.

Let us suppose that the disappearance of atoms takes place according to the scheme outlined in equations VI., VII., and VIII., and that reaction IV. is negligible. If we assume reaction VI. to be irreversible we obtain the equations :

$$[H] = \frac{k_1}{k_6} . I_0 \left[\frac{Cl_2}{O_2} \right] \qquad . \qquad . \qquad . \qquad . \qquad (8)$$

$$\frac{d[ClH]}{dt} = 2k_3 . \frac{k_1}{k_6} . I_0 \frac{[Cl_2]^2}{O_2} \qquad . \qquad . \qquad . \qquad (9)$$

We arrive thus at the equation derived empirically by Bodenstein and Dux. As we have seen the latter represents only an approximation. This arises in the first place from the fact that if the pressure of the hydrogen is of the same order as that of the chlorine, reaction IV. is not completely negligible in comparison with VI. We imagine that in these circumstances the experimental results could be expressed roughly by the relation (3). This theory leads us to expect in particular that, so long as reaction IV. is not quite negligible, the velocity of photosynthesis increases more slowly than the luminous intensity—as Mrs. Chapman has shown. It is besides quite likely that not all the molecules of $H . O_2$ which are formed react with a molecule of H_2 according to equation VII. but that a certain proportion are dissociated before having been able to react. If we represent by k_6' the velocity coefficient of this dissociation, we arrive at the following relationships :—

$$[H] = k_1 . I_0 \frac{[Cl_2]}{[O_2]} . \frac{k_6' + k_7[H_2]}{k_6[H_2]} \qquad . \qquad . \qquad . \qquad (10)$$

$$\frac{d[Cl\,H]}{dt} = 2k_1 k_2 . I_0 \frac{[Cl_2]^2}{[O_2]} . \frac{k_6' + k_7[H_2]}{k_6[H_2]} \qquad . \qquad . \qquad (11)$$

In accordance with these formulæ the velocity of the reaction ought to increase when the pressure of the hydrogen increases beyond a certain limit, in conformity with what has been observed by Mrs. Chapman.

In this way all the experimental facts are explained in an eminently satisfactory manner, and, on the other hand, the scheme we propose leads to certain conclusions on the subject of which experimental figures are lacking. It would be useful, in particular, to verify whether the velocity of reaction is indeed, as foretold by theory, proportional to the square root of the luminous intensity when the proportion of hydrogen in the gaseous mixture is small, and whether the reaction becomes semi-molecular in respect of chlorine when the proportion of hydrogen is extremely low.

In what has appeared above, there is no question of the catalytic influence of water vapour; in regard to this I am absolutely in agreement with the ideas put forward by Professor Bodenstein.

ON THE REACTION BETWEEN H₂ AND O₂ UNDER THE INFLUENCE OF PHOTOCHEMICALLY PRODUCED H-ATOMS AND THE RELATIONSHIP OF ITS MECHANISM TO THAT OF THE BURNING OF DETONATING GAS AT HIGH TEMPERATURES.

By W. Frankenburger and H. Klinkhardt.

A particularly clear conception of the optical sensitisation of photo-chemical gas reactions has resulted from an extension of the fundamental observations of Wood [1] on the extinction of the so-called resonance radiation of metal atoms, especially Hg atoms, by foreign gases.[2]

Franck and Cario [3] have shown that the especially strong quenching influence of hydrogen on Hg atoms which have been excited by absorption of the resonance line 2537 Å., is due to the H_2 molecule taking up energy by collision with the excited metal atom and thereby dissociating into H atoms (collisions of the second kind).

These observations were soon followed by a large number of investigations trying to use the high reactivity of the H atoms so produced for carrying out purely chemical reactions.[4] Among the large number of reactions with such H atoms, *e.g.*, their reaction with CO to aldehydes, with hydrocarbons, etc.—a more quantitative investigation of its action on a hydrogen oxygen mixture appeared to us of value, since the assumption of the assistance of H atoms also lies at the basis of modern ideas on the mechanism of the purely thermal detonating-gas combination at high temperatures. In this reaction, according to these ideas, chain

[1] See *e.g.*, *Phil. Mag.*, **42**, 729, 1922 ; **44**, 538, 1107, 1922 ; *Proc. Roy. Soc.* (A) **97**, 455, 1920 ; **106**, 679, 1924 ; *Z. Physik*, **13**, 353, 1922 ; *Nature*, **115**, 461, 1925 ; *Physical Rev.*, **24**, 243, 1925 ; further J. Franck, *Z. Physik*, **9**, 259 ; **10**, 185, 1922 ; *Ergebn. exakt. Naturwiss.*, **2**, 106, 1923.
[2] Of the many researches on this subject mention may be made of H. A. Stuart, *Z. Physik*, **32**, 262, 1925 ; Oldenberg, *ibid.*, **49**, 609, 1928 ; E. Gaviola, *Physical Rev.*, **33**, 309, 1928 ; **34**, 1373, 1929 ; *Phil. Mag.* (7) **6**, 1167, 1928.
[3] *Z. Physik*, **11**, 161, 1922.
[4] *D.R.P.*, **458**, 756 of the I.G. Farbenindustrie A.G. of 25.9.24 ; Dickinson, *Proc. Nat. Acad. Sci. Wash.*, **10**, 429, 1924 ; H. S. Taylor and A. L. Marshall, *J. physical Chem.*, **29**, 1140, 1925 ; *Nature*, **117**, 267, 1925 ; A. L. Marshall, *J. physical Chem.*, **30**, 34, 1078, 1634, 1926 ; *Z. physik. Chem.*, **120**, 183, 1926 ; F. K. Bonhœffer and Loeb, *Z. physik. Chem.*, **129**, 385, 474, 1926 ; Olson and Meyers, *J. Am. Chem. Soc.*, **48**, 389, 1926 ; H. S. Taylor, *ibid.*, **48**, 2840, 1926 ; Senftleben, *Z. Physik*, **32**, 922, 1925 ; **37**, 529, 1926 ; Klemenc and Patart, *Z. physik. Chem.*, B. **3**, 289, 1929 ; W. Frankenburger, H. Klinkhardt, Ch. Steigerwald, W. Zimmermann, *Z. Elektrochem.*, **36**, 757, 1930.

reactions occur in which H atoms, as well as OH radicals produced from them (according to Haber), play a very essential rôle.[5] In such explosive reactions conclusions about the after supply of the H atoms which start new chains may only be drawn indirectly. The photochemical production of these atoms, on the basis of Einstein's Law of Equivalence, offers, however, the possibility of introducing them in exactly determined quantities into the reaction mixture.[6] In addition, we can induce the photochemical production of H atoms at low temperatures, *e.g.*, room temperatures, and therefore we can also study under these mild conditions the dark reaction following thereon, while the chain reactions of the detonating-gas combustion which are purely thermally set up demand higher temperatures, to which the observation of the secondary processes is consequently limited. It is therefore to be expected that the reaction mechanism may be followed better by the photochemical method than by the purely thermal reaction.

In a more qualitative [7] manner the influence of photochemically produced H atoms on hydrogen oxygen mixtures has already been investigated many times. It was there found that hydrogen peroxide is a product of primary importance in this change. We have in our own work, since 1924,[8] obtained the same result and established the formation of H_2O in addition H_2O_2. Moreover, we tried to obtain an insight into the mechanism of the reaction in a *quantitative* manner.

Experimental Arrangement.

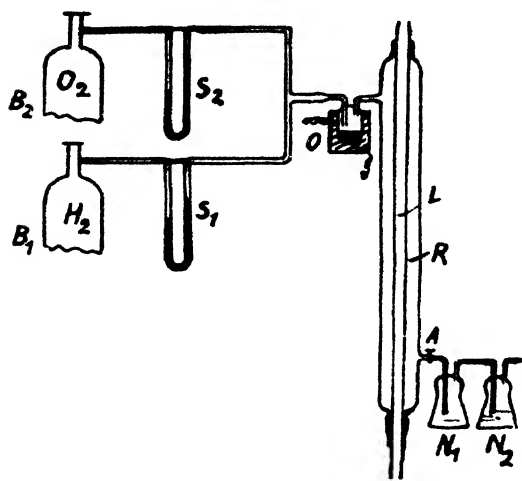Of the two possibilities, the investigation of the reaction statically or dynamically, the latter was chosen, since the H_2O_2 formed can only be prevented from decomposition into H_2O and O_2 (and quantitatively determined), by rapid withdrawal from the reaction zone.

FIG. 1.

Both [9] components H_2 and O_2, after measurement of the velocity of flow by flow manometers (S_1 and S_2), were mixed in the desired ratio and, in a furnace O saturated with mercury vapour at a definite temperature, *i.e.*, laden with Hg vapour of known partial pressure. The sensitised gas now

[5] See *e.g.*, K. F. Bonhœffer and F. Haber, *Z. physik. Chem.*, **137**, 263, 1928.
[6] Compare analogous experiments on the formation of water from $H_2 + O_2$ with H atoms formed photochemically from NH_3: L. Farkas, P. Harteck, F. Haber, *Z. Elektrochem.*, **36**, 711, 1930.
[7] As to the attempt by A. L. Marshall (*J. physical Chem.*, **30**, 1078, 1926) to follow the reaction quantitatively, see further on pp. 435 and 440.
[8] Compare *D.R.P.* 458,756 (25.9.1924), the corresponding work (unpublished) was carried out together with Chr. Steigerwald. Further, a notice in *Z. physik. Chem.*, **B. 8**, 138, 1930, by H. Klinkhardt and W. Frankenburger.
[9] Purification or drying of the gases taken from cylinders was unnecessary ; instead of O_2, five times the amount of air could also be used.

flowed through the reaction vessel R, which (in order to use all the radiation) surrounded the Hg lamp L concentrically and was so deep (2-3 cm.) that the active radiation was absorbed [10] to at least 95 per cent. (measured by absorption spectrograph).

Determination of the Change.

The H_2O_2 produced was absorbed by acidified KI in two wash bottles, in which it liberated the equivalent quantity of iodine titratable by sodium thiosulphate.[11] As is well known, this method is very sensitive, and was quite sufficient to determine the H_2O_2 present to a few parts per thousand of the total gas.

The quantitative determination of the H_2O formed at the same time was much more difficult, as the usual gravimetric method (absorption by $CaCl_2$) is too inaccurate when water is present only to a few thousandths of the total gas, as in this case.

An approximate determination of the H_2O formed was carried out in the following way. In some experiments, in which the gases were circulated in a closed system, the amount of O_2 which had to be added to the gas current to keep the concentration of O_2 constant (H_2 being present in large excess) could be determined approximately. Since in the stationary state exactly the amount added is used for the reaction, the quantity of water formed could be calculated from the oxygen not used in forming H_2O_2. However, the accuracy of this measurement was not great and therefore experiments are in progress for determining the water more accurately by a special titrimetric method.

Blank Experiments.

Before the real investigation it must be proved that the reaction is really initiated by H atoms which are produced by collisions of the second kind with optically excited Hg atoms.

By selective absorption of the resonance line λ 2537 Å. with a bromine or benzene filter (2 per cent. benzene in heptane) the production of H_2O_2 was decreased proportionately with the intensity of this line. A mercury vapour filter also suppressed the reaction, a sign that the direct photochemical formation of H_2O_2, perhaps by way of ozone,[12] was negligible under our experimental conditions on account of the low intensity of the short wavelengths necessary for that reaction. In the case of the omission of the sensitising Hg vapour the reaction ceased completely.

These experiments show that both the resonance line and the Hg atoms, and therefore, according to Franck and Cario,[3] H atoms are necessary for the formation of H_2O_2. Boehm and Bonhoeffer [13] have proved with active hydrogen produced in a Wood tube, that H atoms produced in other ways can also lead to the formation of H_2O_2.

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[10] Compare the absorption measurements carried out by W. Zimmermann (Z. Electrochem., 36, 764, 1930) of λ 2537 Å in the reaction space.

[11] To obtain comparable values it was found useful to express the H_2O_2 yields in g./kw. hour load of the lamp.

[12] Compare Kistiakowsky, J. Am. Chem. Soc., 52, 1868, 1930.

[13] E. Boehm and K. F. Bonhœffer, Z. physik. Chem., 119, 385, 1926.

Stages of the Reaction.

The whole process may be split up into two independent single processes which are coupled through the influence of the sensitiser :—

1. The optical excitation of the Hg atom by absorption of light quanta of the resonance line $\lambda\ 2537$ Å. ($1^1S \rightarrow 2^3P_1$) and the transfer of its energy (7.75×10^{-12} erg per atom or 112 cal. per g. mol.) by collisions of the second kind to the H_2 molecule, which consequently is split into two atoms. In accordance with the large number of researches on these processes, it may be assumed that each absorbed light quantum always leads to the production of two H atoms.

2. The mercury vapour transferring the radiation energy plays a double rôle. On its concentration depends the amount and the spatial distribution of the absorption, and hence of the reaction products.

But it may also itself react chemically with the oxygen.[14] It is, however, shown later [15] that the consumption of both Hg and O_2 by the formation of HgO only influences the main reaction of H_2O_2 formation to quite a negligible extent.

3. The excitation of Hg atoms leads, therefore, mainly to the formation of H atoms, which in turn initiate the dark reaction between H_2 and O_2 leading to the production of H_2O_2 and H_2O. It is to be expected that this dark reaction, in common with every homogeneous gas reaction, can be influenced by concentration velocity of flow, temperature and total pressure.

I. Production and Measurement of H Atoms.

It is known that the intensity of the mercury resonance line $\lambda\ 2537$ Å. depends markedly on the load and cooling of the mercury arc lamp. Since the line is strongly absorbed by Hg vapour (absorption by the vapour in the lamp itself = " self reversal "), it is necessary to make the lamp burn with the least possible vapour pressure, i.e., either with efficient cooling or with low load in a wide tube. At very low vapour pressure ($< 10^{-2}$ mm.) self reversal no longer occurs, and the line intensity decreases rapidly with the pressure as that of most other Hg lines.

Three lamps, constructed according to these principles, proved suitable for the experiments, since they gave relatively intense resonance radiation.

(1) **Externally Cooled Arc Lamp** (Fig. 2).—The arc burns in a quartz tube of 5-10 mm. diameter. The whole burner-tube is enclosed in a wider quartz tube cooled by running water. Load up to 5 amps.

(2) **Incandescent Cathode Lamp** (Fig. 3).—25-40 mm. wide burner tube without cooling. Highest load 1 amp. Since under these conditions a self-maintained arc would not burn, the lamp had an electrically-heated tungsten wire as cathode.

(3) **Internally Cooled Arc Lamp** (Fig. 4).—Burner tube of 25-30 mm. diameter ; a narrow tube of about 7 mm. diameter through which flowed cold water, concentrically inside ; internally cooled iron tube as anode. Load 5-10 amps. Advantages over Nos. 1 and 2 : No absorption of radiation in the cooling water and outer tube : the wide burner tube was, in spite of low mercury vapour density, so warm that neither Hg drops inside nor mercury oxide outside (as in No. 1) precipitated on it.

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[14] See e.g., W. A. Noyes, J. Am. Chem. Soc., **49**, 3100, 1927 ; A. J. Leipunsky and W. Sagulin, Z. physik. Chem., B. **1**,, 362, 1928.

[15] Compare p. 438.

The efficiency of the lamps, measured by the percentage of the electric energy (voltage drop x current) emitted as radiation of λ 2537 Å., increased in the order $1 < 3 < 2$.

All three lamps were fairly long (60-80 cm.) to make the percentage electrode loss as low as possible. They were ignited with the help of a levelling bulb or (No. 2) by means of a " Tefra " (high frequency induction). They gave better results when the cooling water was somewhat preheated (to $30°-50°$ C.).

Measurement of the Resonance Line Intensity.—For the investigation of the dark reaction it was essential to know the number of H atoms produced per unit time. A direct determination of this number was not possible under the given conditions. Owing, however, to the relation that 1 quantum of the line λ 2537 Å. produces 2 H atoms, this
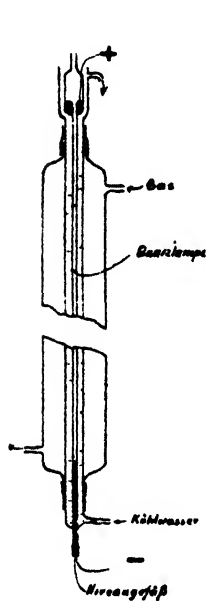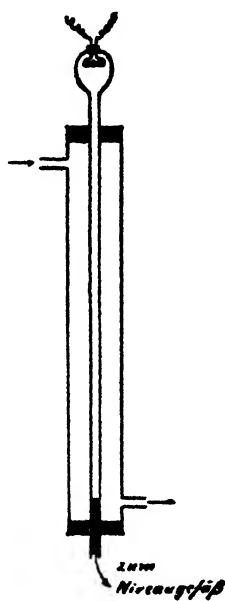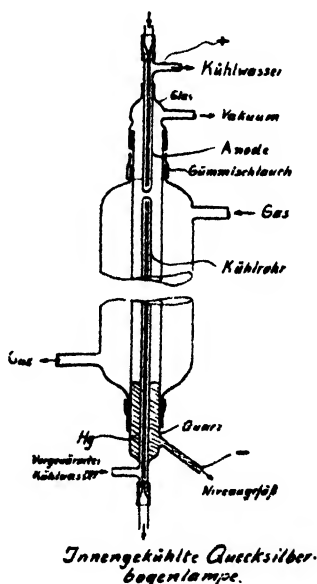
FIG. 2.   FIG. 3.   FIG. 4.

could be replaced by a measurement of the resonance line intensity. The carrying out of this measurement in the usual way with filter, or spectroscopic apparatus and thermopile, involves many possibilities of error, since the absorption loss in the path of the radiation must be allowed for, and the intensity for the whole surface of the lamp must be calculated from measurements [16] on a small part of this path.

Such corrections are entirely eliminated if one can use as measure of the intensity the change produced by the radiation in a photochemical reaction, carried out in the same reaction vessel as the production of H_2O_2. Certainly, such a reaction must fulfil the conditions that it responds practically only to the line investigated, that it leads to no back or side reactions, that the proportionality factor between radiation intensity and chemical change, e.g., in the form of the quantum efficiency

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[16] Measurements of this sort were carried out by A. L. Marshall, *J. physical Chem.*, **30**, 1078, 1926.

$\phi = \dfrac{\text{number of changed molecules}}{\text{quanta}}$ is accurately known, and that the charge can be accurately determined.

Fortunately all these conditions are fulfilled for λ 2537 Å. by the hydrolysis of monochloracetic acid.

$$CH_2Cl\ COOH + H_2O \rightarrow CH_2OH\ COOH + HCl$$
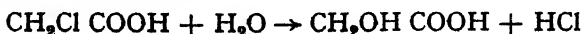
According to the investigations of E. Rudberg,[17] which were confirmed by our own measurements, this reaction has the quantum efficiency $\phi = 1 \cdot 0$ for λ 2537 Å. : immediately adjacent (as well as shorter) wavelengths act similarly, but their intensity, in the case of the lamps described, was negligible compared with that of λ 2537 Å. Up to considerable change of the monochloracetic acid strict proportionality to the absorbed quantity of light was observed without back or side reaction. The accompanying thermal hydrolysis was quite negligible below 50°, and could easily be taken into account above.   The amount of hydrolysis was determined by titration with $AgNO_3$ of the hydrochloric acid formed, the end point being very accurately detected electrometrically.

For the measurement, the whole reaction vessel round the lamp was filled with 0·5 N aqueous monochloracetic acid.   At this concentration the resonance line was practically completely absorbed (according to spectroscopic estimation > 95 per cent.) as in the case of gas sensitised with Hg vapour.   After the illumination, which took place under vigorous stirring with nitrogen, the number of HCl molecules formed and hence the absorbed and emitted quanta of the resonance line, could easily be determined.

The lamps used radiated several per cent. of the electrical energy input as resonance light (No. 1 up to 3 per cent., No. 3 up to 5 per cent., and No. 2 up to 10 per cent.)[18].   These efficiencies varied with load and temperature of the cooling water quantitatively in the expected manner.

II. The Efficiency of the Sensitiser.

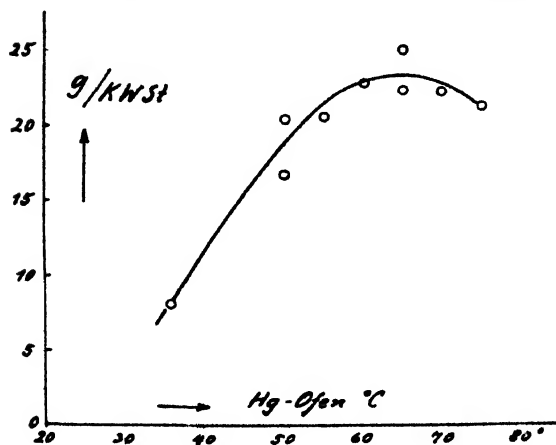The concentration of the mercury vapour could easily be varied by the temperature of the Hg furnace.   It was found that the yield of H_2O_2 depends very much on the partial pressure of the mercury and reaches a maximum for a temperature of the furnace O of 60°-70°, corresponding to a pressure $p \cong 0 \cdot 035$ mm. Evidently here two influences are working against each other. (Fig. 5.)

At low pressures the absorption of light is incomplete, while at

FIG. 5.

[17] E. Rudberg, Z. Physik, 24, 247, 1924. Dr. Weyde, Oppau, kindly drew our attention to this article.

[18] In contrast with these the usual uncooled Hg lamps work with a " yield " of resonance radiation of only a few parts per thousand.

higher mercury concentrations the dark reaction is crowded into a small space near the lamp which may lead to disturbing wall effects, *e.g.*, recombination of H-atoms.

III. The Dark Reaction.

Keeping the conditions for the production of H atoms (kind, load and temperature of the lamp, partial pressure of the mercury) as constant as possible, the dependence of the dark reaction, the H_2O_2 yield (in g./kw. hour) on *temperature, pressure, concentration of oxygen* and *velocity of flow* was investigated.

It turned out that temperature (about 50°-200° C.)[19] and pressure (1-11 atm.) had no influence on the yield of H_2O_2, while the latter increased rapidly with both other variables (Figs. 6 and 7). It was remarkable, how-
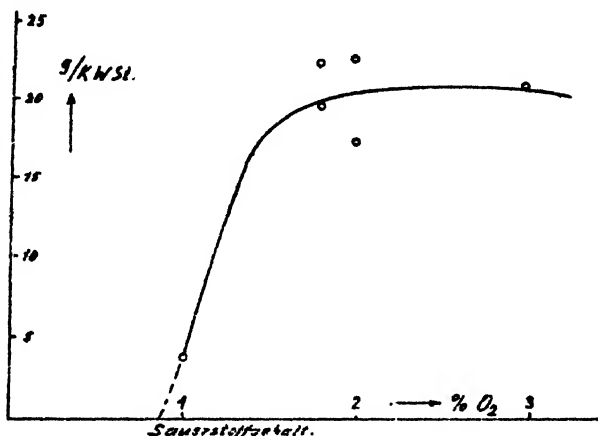
FIG. 6.

ever, that in both cases the yield after reaching a certain value could not be further increased by further increase of the variables. This maximum value had in both cases the same magnitude of about 20-25 g./kw. hour (for lamp No. 3), and was reached with a flow velocity of about 2 cubic metres gas per hour and an oxygen content of about 2 per cent. An increase of the O_2 concentration above 3 per cent. even causes further a diminution of the yield, since then considerable quantities of HgO are precipitated on the walls and partly screen off the radiation and decompose the H_2O_2. It is certain
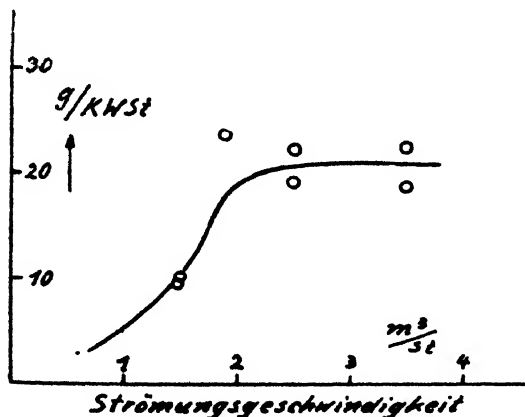

FIG. 7.

that this limiting value of the yield, which was never passed, has a special significance for the reaction.

[19] Blank experiments, in which concentrations of H_2O_2 equal to those in the reaction mixture, in the absence of impurities, did not decompose appreciably in the gas stream up to 200°, showed that the constancy of yield cannot be explained by an accidental compensation of higher velocities of formation and decomposition.

Evidently under these conditions all inhibiting influences are eliminated, and all side reactions practically completely cut out. Since in this case the conditions are specially clear and simple, the quantum efficiency $\phi = \dfrac{H_2O_2 \text{ molecules formed}}{\text{quanta absorbed}}$ was determined for the limiting value as a characteristic case. It could easily be calculated if a reaction was always carried out with the gas mixture and with monochloracetic acid successively, keeping the operating conditions of the lamp as constant as possible. Then simply $\phi = \dfrac{\text{Number of } H_2O_2 \text{ molecules}}{\text{Number of Cl' ions}}$ both referring to the same lamp current.

A value between 1 and 2 (mean about 1·2) was obtained, of which the larger values are the more reliable, since the systematic error (contamination of the lamp walls by HgO, decomposition of H_2O_2) can only decrease the quantum efficiency. (Fig. 8.)
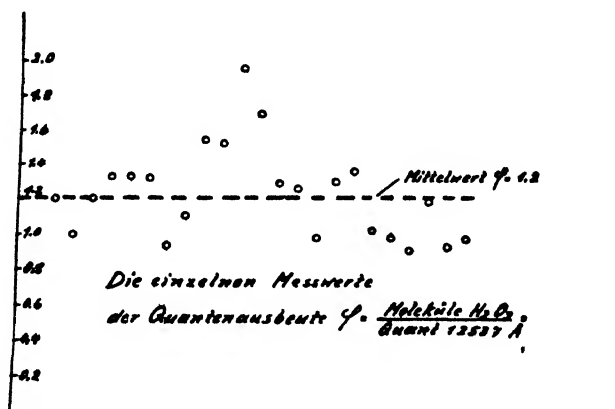

FIG. 8.

Quantitative Data on the Consumption of Oxygen and the Part Played by Mercury Atoms.

The maximum yield (limiting value) of about 20 g./kw. hour of H_2O_2 was reached with a flow velocity of 2000 litres/hour H_2 and 40 litres/hour O_2 (corresponding to a partial pressure of 15 mm.). The irradiated gas contained accordingly, for a lamp load of 0·3 kilowatt, 6 g. H_2O_2 per hour corresponding to a partial pressure of 1·5 mm. and a consumption of 10 per cent. of the irradiated oxygen. About 6 g./hour H_2O, i.e., double volume was found by the method described. If the gas at 60° C. was saturated with Hg vapour (partial pressure $p = 0\cdot035$ mm.), it contained about 0·005 per cent. mercury vapour, which by complete oxidation to HgO would consume, at the most $\dfrac{0\cdot035}{15 \times 2} \times 100$ 0·1 per cent. of the oxygen. This value lies within the experimental error of the method used. Since the partial pressure of the H_2O_2 formed is forty times greater than that of the mercury, and the quantum efficiency $\phi = 1 - 1\cdot5$ H_2O_2 molecules per quantum, each Hg atom must transfer, on the average, the energy of from 30 to 40 light quanta to H_2 molecules before it is finally oxidised to HgO or leaves the reaction space. But

this means that the oxide formation is to a large extent unimportant and cannot hinder appreciably either the H_2 dissociation by excited Hg atoms, or the consequent dark reaction.

Discussion of Experimental Results.

Our measurements lead to the result that photochemically produced H atoms induce in hydrogen oxygen mixtures at room temperature, secondary reactions in the course of which about one H_2O_2 molecules and $2H_2O$ molecules are formed per quantum λ 2537 Å. absorbed [20] (corresponding to two primarily-produced H atoms). Ideas on the nature of the processes leading to the formation of H_2O_2 and H_2O from H atoms, have already been developed by various authors. For their discussion a closer knowledge of the heat effects of the suggested stages of the reaction is necessary. We shall use for the calculation the following data, differing somewhat from previous values owing to newer values for the energy of dissociation of oxygen.[21]

(1) $H + H \rightarrow H_2 + 100$ Cal.[22].
(2) $O + O \rightarrow O_2 + 117$ Cal.[23].
(3) $OH + H \rightarrow H_2O + 111$ Cal.[24].
(4) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 57$ Cal.
(5) $H_2 + O_2 \rightarrow H_2O_2 + 38$ Cal.[25].

From this result the following values :
(a) for the step by step synthesis of H_2O_2

(6) $H + H + O + O \rightarrow H_2O_2 + 255$ Cal.
(7) $H + H + O_2 \qquad \rightarrow H_2O_2 + 138$ Cal.

(8) $H + O_2 \qquad \rightarrow HO_2 + 69$ Cal.
    $H + HO_2 \qquad \rightarrow H_2O_2 + 69$ Cal.

                        assuming that process (7) may be split into two thermally similar steps.[26]

and

(b) for the step by step synthesis of H_2O

(9) $H + H + O \qquad \rightarrow H_2O + 215$ Cals.
(10) $H + O \qquad \rightarrow OH + 104$ Cals.

Using these data we will consider the following reaction schemes :—

1. **The H_2O_2 Chain.**—In 1926 A. L. Marshall [27] carried out an investigation with the same aim as ours in which he determined the absorption of quanta in the reaction mixture in an indirect way, which

[20] The relatively small deviations from this result, which are in the sense that the quantum yields of H_2O_2 are sometimes higher than 1 (up to about 1·5) and those of H_2O sometimes lower than 2 (to about 1·5), will be considered at the end of the discussion, but are neglected for the moment.
[21] Compare L. Farkas, F. Haber and P. Harteck, *Z. Elektrochem.*, **36**, 711, 1930. The heats of reaction should be accurate to ± 10 cal.
[22] H. Groner, *Erg. exakt. Naturwiss.*, **6**, 75, 1927 ; R. T. Birge, *Proc. Nat. Amer. Acad.*, **14**, 12, 1928.
[23] G. Herzberg, *Z. physik. Chem.*, B. **10**, 189, 1930 ; W. P. Baxter, *J.A.C.S.*, **52**, 3468, 1930.
[24] K. F. Bonhoeffer and Reichardt, *Z. Elektrochem.*, **34**, 652, 1928 ; F. Haber and K. F. Bonhoeffer, *Z. physical Chem.*, **137**, 264, 1928.
[25] V. Wartenberg and Sieg, *Ber.*, **53**, 2192, 1930.
[26] See also Urey, Dawsey and Rice, *J.A.C.S.*, **51**, 1371, 1929.
[27] *Z. physik. Chem.*, **30**, 1078, 1926.

in our opinion is less certain.   He concluded from these measurements a high quantum efficiency, namely 6 to 7 molecules per absorbed quantum for the formation of H_2O_2.   Therefore the formation of each H atom must be followed by a chain reaction in which several H_2O_2 molecules are formed.   Marshall takes as probable the following scheme :

$$(\alpha) \quad H + O_2 \rightarrow HO_2$$
$$(\beta) \quad HO_2 + H_2 \rightarrow H_2O_2 + H, \text{ etc.}$$
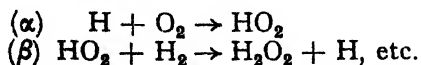
The assumption of a combination in the gas phase according to α meets difficulties [28] because of the problem of disposing of the heat of reaction. Another indication against this process is that, so far, a compound HO_2 has never been observed, even in band spectra.[29]   Moreover, the reaction step β would be endothermic (— 31 cal.), whereas the reaction

$$HO_2 + H_2 \rightarrow H_2O + OH$$

would be exothermic (+ 33 cal.).[30]   This makes improbable Marshall's scheme of a chain producing H_2O_2 ; so does, even more, our proof that the quantum efficiency calculated on H_2O_2 is not essentially greater [31] than 1.

2. **The H_2O Chain.**—More recently Hinshelwood, and Haber with co-workers, have carried out exact investigations on the kinetics of the homogeneous thermal detonating-gas combination at higher temperatures.   They found this process to be a chain reaction in the region where it takes place explosively, that is at temperatures about 400°. Each single chain, once started, thus produces a large number of water molecules.   Following up older work on the theory of combustion processes, and newer spectroscopic observations by K. F. Bonhœffer and F. Reichardt, who showed the presence of OH in hydrogen flames, F. Haber has given the following scheme of the chemistry of this chain reaction :—[32]

$$(\gamma) \quad H + O_2 + H_2 \rightarrow H_2O + OH.$$
$$(\delta) \quad OH + H_2 \rightarrow H_2O + H, \text{ etc.}$$
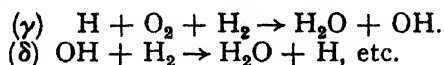
Reaction γ is exothermic, with 102 calories, therefore very favoured thermodynamically.   The stage δ has only a relatively small heat production, 11 calories, according to the above data, but is not improbable, either, from the purely thermodynamical point of view.

In principle, starting from the formation of a single H atom, a great number of H_2O molecules can be formed by frequent repetition of steps (γ) and (δ).   Further, the possibility exists that two OH radicals formed in the reaction step γ may combine to a molecule of H_2O_2 :—

$$(\epsilon) \quad 2OH + M \rightarrow H_2O_2 + M + 19 \text{ cal.}$$
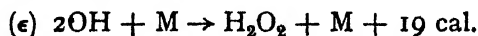
[28] Compare K. F. Herzfeld, *Z. Physik*, **8,** 132, 1922 ; *Z. Elektrochem.*, **25,** 301, 1919 ; M. Polanyi and E. Wigner, *Z. Physik*, **33,** 429, 1925 ; M. Born and J. Franck, *Ann. Physik*, **76,** 125, 1925.
[29] Compare F. Haber and K. F. Bonhœffer, *loc. cit.*, p. 270, n. 1.
[30] In other words, H_2O_2 cannot be formed in one elementary process at the same time as a hydrogen atom but would react with it to form ($OH + H_2O$) with considerable liberation of energy.
[31] An indirect proof that, as a mean, only one H_2O_2 molecule is formed per hydrogen atom given by the electrochemical current efficiency of cathodic formation of H_2O_2.   The yield is then about 80 to 90 per cent. of the theoretical that is 0·8-0·9 mols. H_2O_2 formed per mol. of H atoms liberated at the cathode.
[32] Compare also the exhaustive discussion of the possibilities of the reaction by E. H. Riesenfeld and E. Wassmuth, *Z. physik. Chem.*, A. **149,** 140, 1930.

This means a break in the corresponding Haber chain, since the OH radicals are removed and can take no further part in δ. Under reaction conditions in which other chain breaking factors play a relatively small rôle, and all chains end through combination of two OH radicals, then, according to this scheme, the number of H_2O_2 molecules produced will be half the number of H atoms primarily formed, i.e., the quantum yield of H_2O_2 is always equal to 1 under these circumstances.

The agreement of this conclusion from Haber's scheme with our experimental results suggests that the H_2O_2 formation really takes place through reactions characterised by the above scheme. However, the quantum yield of H_2O_2 gives no information whether, besides the peroxide formation, H_2O producing chains also take place and, if so, how long these chains are. This question can only be answered by measurements of the photochemical yield of H_2O. Our experiments on this point show that the amount of water formed does not exceed very much that given by co-operation of the processes (γ) and (ε) only, i.e., about $2H_2O$ molecules for each H_2O_2. Consequently we think we have proved that *at room temperature the process δ does not take place to an extent worth mentioning.*

In a recent paper F. Haber also arrives at the same conclusion from experiments on the ignition of detonating gas mixtures with H atoms photochemically produced from NH_3.

We therefore conclude that at room temperatures the chain promoting process (δ) compared with the union of two OH radicals is of very little importance. At temperatures of about 400° C., however, it apparently becomes very noticeable. From this increase of the probability of reaction with increasing temperature, it may be concluded that the process $OH + H_2 \rightarrow H_2O + H + \backsim$ 11 Cal. requires a considerable energy of activation Q. The magnitude of Q could be obtained by determination of the quantum yield at different temperatures, calculating Q from the temperature coefficient in the usual way.[33]

An indication of the *lower* limit of Q can be obtained from the fact that any water formed in excess of the amount of the two molecules per quantum given by process (γ) is so little that it is within the limits of accuracy of our analyses. Hence $Q \gtrless 14$ Cal.

For the calculation of $Q_{minimal}$ it is necessary to know the concentration C of OH radicals when this has reached a stationary value in the reaction mixture. If N is the number of quanta absorbed per sec. per c.c., the number of H atoms and OH radicals formed per sec. per c.c. is equal to $2N$. If further the decrease of C is determined by the number of ternary collisions of the type (OH + OH + H) in such a way that each three body collision leads to the formation of one H_2O_2 molecule, then for the stationary state

$$+ \frac{d[OH]}{dt} = - \frac{d[OH]}{dt};$$

$$2N = 2Z . C^2 . \qquad . \qquad . \qquad . \qquad . \qquad (i)$$

After substitution of the values [34, 35] for N and Z :

by substituting these values in equation i : $2 \times 10^{16} = 2 \times 10^{33} \times C^2$,

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[33] Compare, e.g., C. N. Hinshelwood, *Kinetics of Chemical Changes in Gaseous Systems*, p. 40.

[34] N is calculated for a certain lamp (Type 3, Load $\sim$ 250 watt, experiment No. 182) in the following way. The total number of quanta λ 2537 Å emitted,

whence $C \cong 3 \times 10^{-9}$ g. mols., present in 1 c.c. in the stationary state (partial pressure of OH $\sim 6 \times 10^{-2}$ mm).

Since about 4×10^{-5} g. mol. H_2 are present in 1 c.c. of the reaction mixture the number Z of collisions per c.c. between OH and H_2[36] at

$$T = 330° \text{ Abs.}$$

is

$$Z = \pi \sigma^2_{H_2 + OH} n_{H_2} n_{OH} \sqrt{\bar{u}^2_{H_2} + \bar{u}^2_{OH}},$$

and after substituting the values

$$\sigma_{H_2} = 1\cdot2 \text{ Å}[37] \qquad \sigma_{OH} = 1\cdot1 \text{ Å}[38],$$

$$n_{H_2} = 4 \times 10^{-5} \times 6 \times 10^{23}$$

$$n_{OH} = 3 \times 10^{-9} \times 6 \times 10^{23}$$

$$\bar{u}^2_{H_2} = 348 \times 10^8$$

$$\bar{u}^2_{OH} = 41 \times 10^8$$

$$Z = 3\cdot1 \times 5\cdot3 \times 10^{-16} \times 4 \times 10^{-5} \times 3 \times 10^{-9} \times 36\cdot10^{46} \sqrt{348 + 41}$$
$$= 1\cdot2 \times 10^{25}$$

If, therefore, a considerable fraction of collisions between OH and H_2 result in the reaction δ, a very considerable quantity of H_2O above the amount of 2 molecules per quantum given by process γ would be formed.[39] On the other hand, the determination of the water actually formed shows that it never exceeds 2 molecules per quantum by more than 50 per cent. This statement may be regarded as certain within the limits of accuracy of the methods of analysis.

In experiment No. 182, used as the basis of this calculation, 2×10^6 c.c. of reaction mixture flowed through a vessel of $1\cdot5 \times 10^3$ c.c. capacity, remaining therein for a mean time of 3 seconds and produced ~ 5 gms. H_2O_2 and $\hookrightarrow 5$ gms. H_2O. This means that any additional water formed will be at most $\cong 2\cdot5$ gms. Hence the possible number of H_2O molecules formed by reaction δ is certainly less than $1\cdot6 \, 10^{16}$ per sec. per c.c. Using the calculated value of the number of collisions Z we have :—

Maximum efficiency of collisions $< \dfrac{1\cdot6 \times 10^{16}}{1\cdot2 \times 10^{25}} \cong 1\cdot3 \times 10^{-9}$. Since

$1\cdot3 \times 10^{-9} = e^{-21\cdot6}$, $\dfrac{Q}{RT} \gtrless 21\cdot6$. For $T = 330°$ Abs., this gives

$$Q \gtrless 21\cdot6 \times 0\cdot66 \text{ Cal.,}$$

that is, $\qquad\qquad\qquad Q \gtrless 14$ cal.

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and absorbed in the reaction vessel, is $\sim 2 \times 10^{18}$ per sec. This number is absorbed in $1\cdot5 \times 10^3$ c.c. of the reaction mixture (volume of the reaction vessel) that is $\sim 1 \times 10^{15}$ quanta per c.c. The experimental decrease of radiation intensity in the path of the radiation causes a decrease of the concentration of photochemical primary products with increasing distance from the source of light. This is allowed for in this rough calculation by taking a mean value.

[35] The number S of *binary* collisions $(OH) + (OH)$ in 1 c.c. at 330° Abs. is given by $S = \sqrt{2}\pi r^2_{OH} \bar{u}_{OH} \cdot C^2 N)^2$; for $r = 1\cdot1$ Å. and $\bar{u}_{OH} = 64000$ cm./sec. $S \cong 1\cdot10^{37}C^2$. The number Z of *ternary* collisions $(OH) + H_2$ is about 10^{-4} of this, since the molecular volume of the 4×10^{-5} g. moles of H_2 present in 1 c.c. is $4 \times 10^{-5} \times 7 \times 10^{-24} \times 6 \times 10^{23} \cong 1 \times 10^{-4}$ c.c. Hence
$$Z = S \times 10^{-4} \cong 1 \times 10^{33} \times C^2.$$

[36] C. N. Hinshelwood, " Reaktions Kinetik gasförmiger Systeme, deutsche Übersetzung von E. Pietsch u. G. Wilke " (*Akad. Verlagsges*, Leipzig, 1928), S. 47.

[37] See Landolt-Börnstein, 5 Edn., 1, 169.

[38] Owing to the similarity between OH and Cl the radius of the latter was taken instead of the unknown value for the former (see Landolt-Börnstein according to Goldschmidt, 2, 68.

[39] The amount of oxygen present in the reaction mixture is quite sufficient for such an increased production, *e.g.*, in some experiments 90 per cent. of the total amount of oxygen passed the reaction vessel unchanged.

We believe that we have a certain amount of confirmation of this Q value in the value calculated from the temperature coefficient of the photochemically sensitised detonating gas combination. L. Farkas, F. Haber and P. Harteck,[40] using H atoms, produced from NH_3, found a factor 2 for a temperature increase of 30°-35° in the neighbourhood of 570° Abs. corresponding to an energy of activation $Q = 16$ cals.

Assuming a Q-value of 14 Cal., a calculation of the efficiency of collisions in the reaction $OH + H_2 \rightarrow H_2O + H$ in the region where explosion starts (*i.e.*, about 680° Abs.) showed that on the average *one collision in* 10^4 to 10^5 *must be effective*. The atoms and molecules (H, OH), which break the chains are present in a concentration of about 10^{-8} to 10^{-9} g.mol./c.c. and the H_2 molecules, which continue the chains, to about 10^{-5} g. mol./c.c. Ternary collisions (factor $\leftharpoonup 10^{-4}$) are necessary for the ?recombination processes (H + OH) and (OH + OH) and the collision efficiency of the reaction (OH + H_2) is 10^{-5} at the lower explosion reaction limit. The ratio of the number of OH radicals reacting in a way which breaks the chain to the number continuing chains is consequently

$$\frac{10^{-8} \times 10^{-4}}{10^{-5} \times 10^{-4}} = 10^{-3}.$$

This value may be too small, since chains may end on the walls. Since, therefore, one chain-breaking process occurs for 100 to 1000 which continue chains, a chain will have 100 to 1000 links. This also agrees with the results of Haber and co-workers.

Finally the very small efficiency of collisions at $\leftharpoonup 300°$-$400°$ (in consequence of the large energy of activation Q) could also explain the long induction periods between the primary formation of H atoms and appreciable combination of detonating gas, observed by Haber and co-workers.

The fact that the reaction (OH + H_2) requires a considerable energy of activation is in agreement with the fact that the same is true for (Cl + H_2) and (Br + H_2), while the reactions (H + Cl_2) and (H + Br_2), as well as, apparently (H + $(HO)_2$) take place spontaneously.[41]

While the *water formation* which follows the photochemical primary reaction is, at least for the most part, strongly dependent on temperature, this is *not true for the H_2O_2 formation*. Hence we conclude that the reaction steps (γ) and (δ) leading to the formation of H_2O_2 are independent of temperature (in other words, need no energy of activation), and also that the OH radical must be relatively stable. Researches on the reaction between H_2 and CO induced by H atoms [42] have shown that not all radicals occurring as intermediate products in photochemical gas reactions are stable, since the radical HCO was found to be very sensitive to temperature. This difference might be due to the very different heats of formation of the two radicals

$$(OH \leftharpoonup 104 \text{ Cal. } HCO \leftharpoonup O \text{ Cal.}).[43]$$
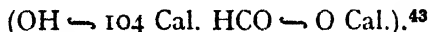
An attempt was also made to obtain the absorption spectrum [44] of the OH radicle, using continuous ultra-violet radiation lengthwise in the reaction vessel. These experiments gave a negative result.

[40] *Z. Elektrochem*, **36**, 711, 1930 ; *Naturwiss.*, **18**, 266, 1930.
[41] Compare M. Polanyi and Hartel, *Z. physik. Chem.*
[42] W. Frankenburger, H. Klinkhardt, Ch. Steigerwald and W. Zimmermann, *loc. cit.*, 4.
[43] Compare R. Mecke, *Z. physik. Chem.* (B) **7**, 108, 1930 ; *Nature*, **125**, 256, 1930 ; *Z. Elektrochem.*, **36**, 7, 1930.
[44] Carried out by W. Zimmermann.

No absorption in the region of the OH bands [45] could be detected.[46] Apparently the concentration of the radical ($\backsim 10^{-2}$ mm.) is too small to make this proof possible. However, it was possible to obtain the OH bands and the continuous spectrum of H_2O_2 in emission, from reacting H_2/O_2 mixtures of sufficiently low pressure photochemically sensitised with Hg vapour, probably in consequence of the more frequent excitation of OH radicals by excited Hg atoms under these conditions. The increase of quantum yield of H_2O_2 above 1 to the value 1·5 and the decrease of that of H_2O from 2 to the same value, which must be regarded as experimentally certain, will now be considered. It is conceivable that these changes in yield are due to the substitution of the reaction steps (γ) and (ϵ), producing 1 H_2O_2 and 2H_2O molecules per quantum, by the reaction steps

$$(\eta) \quad H + H_2O + O_2 \rightarrow OH + H_2O_2 + 27 \text{ Cal.}$$

followed by

$$(\epsilon) \quad 2(OH) + M \rightarrow H_2O_2 + M,$$
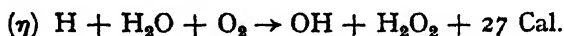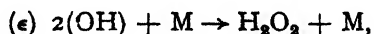
which yield 3H_2O_2 and no H_2O per quantum. Since reaction η needs the co-operation of water it will be relatively favoured in gases containing H_2O. This is in agreement with the result that in those experiments in which the gases were circulated and, in consequence of the use of aqueous solutions to absorb the H_2O_2, had a considerable water content, these deviations occurred to a greater extent. For instance, in such an experiment 70 per cent. of the total O_2 consumption was used for H_2O_2 formation and 30 per cent. for water formation, i.e., about equal numbers of H_2O_2 and H_2O molecules were formed. Consequently the " normal " reaction with a quantum efficiency of 1 for H_2O_2 has taken place to the extent of 75 per cent. and that with quantum efficiency 3 to 25 per cent., giving an over-all value of $\backsim$ 1·5. This is in good agreement with the higher values of the series of directly determined quantum yields.

[45] Bonhoeffer and Reichardt, *Z. Elektrochem.*, **34**, 652, 1928 ; *Z. physik. Chem.* (A), **139**, 75, 1928.
[46] However the absorption bands of H_2O_2 were quite distinct.

GENERAL DISCUSSION.

Mr. G. R. Gedye (*Cambridge*) said : It is interesting to compare the results of Dr. Frankenburger on the photo-sensitised formation of hydrogen peroxide and water with those of the corresponding reaction due to gaseous ions. Scheuer[1] investigated this reaction under the action of α-particles and his results show that 3·7 molecules of water were formed per ion pair, the intermediate formation of hydrogen peroxide being noted. The value is in good agreement with that of Lind[2] who found $M/N = 3·85$. The use of high speed electrons from a Lenard tube enabled Marshall[3] to examine the initial stages of the reaction in much greater detail. Hydrogen peroxide, water and ozone were primary products. Hydrogen peroxide was the principal product with a large excess of hydrogen, while water and ozone predominated when oxygen was in excess.

The work of Brasefield[4] shows that the primary ionisation process in

[1] *Compt. Rend.*, **159**, 423, 1914.
[2] *J.A.C.S.*, **41**, 531, 1919.
[3] *Ibid.*, **50**, 3178, 1928.
[4] *Physical Rev.*, **31**, 52, 1928.

hydrogen is the formation of an H_2^+ ion, which except at very low pressures gives H^+ and H by collision. At higher pressures the H_3^+ ion predominates. Dissociation into $H_2 + H$ or possibly $3H$ must occur on recombination with an electron. This means that the net effect of ionisation in hydrogen is the formation of not less than two H atoms per ion-pair. Consequently one would expect to observe in hydrogen-oxygen mixtures, effects similar to those of the photosensitised reaction, complicated by the results of ionisation and possible dissociation of the oxygen molecule. The ion-pair efficiency would be expected to be the same or slightly higher than the quantum efficiency. Actually the values of 3·7 and 3·85 for M/N, where M refers to the total water eventually formed, are in good agreement with Dr. Frankenburger's value of between 1 and 2 for hydrogen peroxide alone. They are further in agreement with the proposed mechanism of reaction. The well-known formation of OH in the discharge tube further supports the similarity of the mechanism of the formation of hydrogen peroxide in the two cases. Thus the work on the hydrogen-oxygen reaction due to gaseous ions provides an interesting confirmation of Dr. Frankenburger's work.

Dr. Frankenburger, in reply, said : I am glad to have this interesting reference to the analogy between the photochemical production of hydrogen peroxide and that brought about by ionisation by collision. A similar analogy exists in the case of the production of formaldehyde and glyoxal from hydrogen and carbon oxide, on the one hand photochemically, and on the other by means of collision ionisation with the silent discharge. It seems to me that in the method of production by collision ionisation there is a certain complication, in that to a greater extent the *product of reaction*, such as hydrogen peroxide, formaldehyde, etc., are more apt to be destroyed than in the case of the specific photochemical method mentioned. It appears, moreover, that the energy yield in respect of formation of hydrogen peroxide in the photochemical case amounts to about double that obtainable with the silent electrical discharge. Presumably this is due to a secondary destruction of the hydrogen peroxide by ionic or electronic collision in the latter case.

THE PHOTOCHEMICAL UNION OF HYDROGEN AND CHLORINE AT LOW PRESSURES.

By J. B. Bateman and H. C. Craggs.

Trifonoff[1] recently claimed that an equimolecular mixture of hydrogen and chlorine will not combine in light if the total initial pressure of the gases is less than 0·4 mm. Trifonoff's curves also show that this limiting pressure is higher the greater the initial pressure of the gases, thus implying inhibition by the hydrogen chloride produced in the reaction. The first result conflicts with the earlier work of Marshall,[2] who found that although the quantum efficiency decreased rapidly as the pressure was lowered, a definite reaction occurred when the pressures of both hydrogen and chlorine

[1] Trifonoff, *Z. physik. Chem.*, B6, 118, 1929.
[2] Marshall, *J. physical Chem.*, 29, 1453, 1925.

were considerably below o·2 mm.   Rollefson[3] studied the kinetics of the
reaction with a chlorine pressure of 1·4 mm. and hydrogen pressures vary-
ing from o·078 mm. to o·0007 mm., finding under these conditions that
the rate of reaction was proportional to the hydrogen pressure.   Hence if
Trifonoff's result is correct, the determining factor in the sudden stoppage
of reaction must be the chlorine pressure alone.

The object of the experiments described in this paper was to test the
accuracy of Trifonoff's statement, using the simplest possible technique
and at the same time properly controlled conditions.   The method finally
used, after much consideration, was to follow the reaction by measuring
the hydrogen pressure, the chlorine being kept at constant concentration
by contact with solid chlorine at an appropriate temperature.

The method of measuring the hydrogen pressure that suggested itself
was the use of an ordinary tungsten filament Pirani gauge ; it was thought
possible that if dry gases were used, and the gauge filament only heated
when the chlorine was frozen out with liquid air, corrosion of the filament
might be avoided.   A glass-covered filament, such as that described by
Rollefson,[4] would then be unnecessary.   Experiment bore out this expec-
tation.

Calibration of the Pirani Gauge for Hydrogen.

A calibration of the gauge was necessary for these experiments.   This
was made by taking a parallel series of readings on the Pirani gauge and
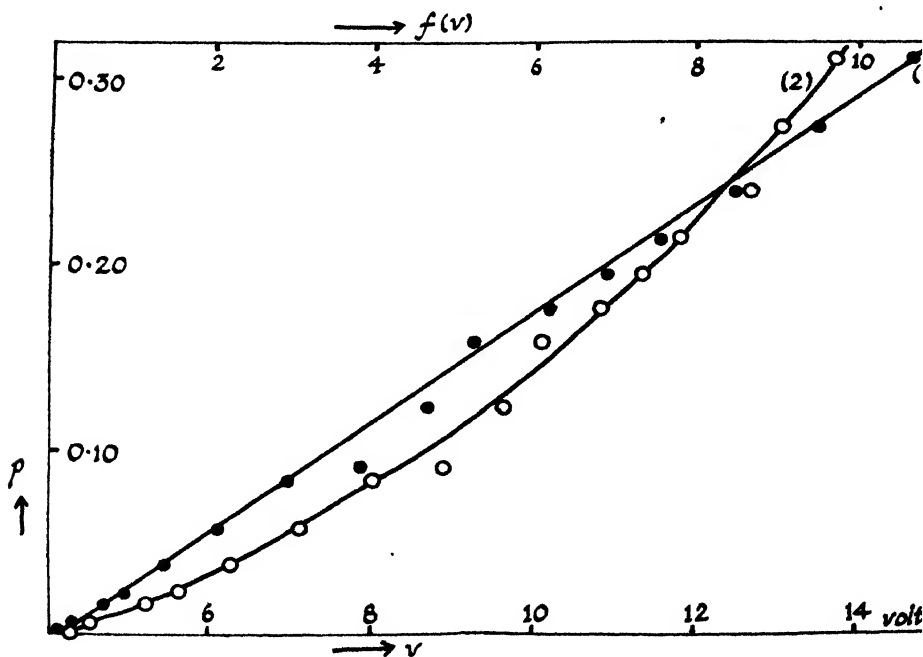
Fig. 1.   (1) $p - f(v)$; (2) $p - v$.

a calibrated McLeod gauge at varying hydrogen pressures.   The calibra-
tion data are summarised in Fig. 1.   Curve 2 shows the gauge reading in

[3] Rollefson, *J. Amer. Chem. Soc.*, 51, 770, 1929.   [4] *Ibid.*, 804, 1929.

volts, v, as a function of the pressure, p, and curve 1 is the plot of p against $f(v)$, where

$$p = \frac{a(v^2 - v_0{}^2)}{v_0{}^2} = a \cdot f(v)$$

v_0 being the gauge reading for zero pressure and a is the gauge constant.

Pure hydrogen was prepared by electrolysis of caustic soda solution in an apparatus which gave a supply of the gas that had been in contact only with glass, the electrolytic solution, and the nickel cathode. Traces of oxygen were removed by heated palladised asbestos, and the gas dried by phosphorus pentoxide.

Apparatus and Procedure.

Fig. 2 shows diagrammatically the disposition of apparatus employed in the majority of the experiments. It was made entirely of soda glass, and was designed to prevent any possible contamination of chlorine with tap grease.

a is the Pirani gauge sealed on to wide glass neck b communicating with c, the insolation chamber which is a cylindrical vessel with flattened ends,
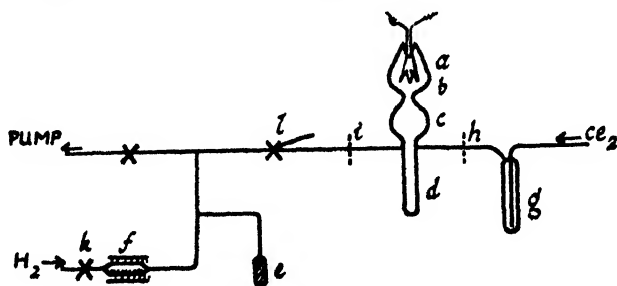
FIG. 2.

12 cm. long $\times$ 3 cm. diameter. d is the chlorine reservoir. The inlet tube on the left leads to the vacuum train, hydrogen generator, and the tube e, containing an activated charcoal. f is a tube of palladised asbestos. The tube on the right leads through the liquid air trap g back to the chlorine cylinder, to which it is connected by a metal-glass joint.

In two preliminary experiments a slightly different arrangement of liquid air traps was used, and the experimental procedure was not the same as in the experiments described below; it is only necessary to mention here that the modifications were made in order to avoid difficulties in freeing the cylinder chlorine from a volatile impurity—probably HCl—which was present in rather large amounts. The final procedure was as follows :—

(1) The whole apparatus was evacuated and baked out by cautious warming with a Bunsen flame until the Pirani gauge reading was no longer changed on surrounding the tube d with liquid air. The final reading, v_0, was noted.

(2) With a bath of melting methylcyclohexane (146·6° K.) surrounding d and liquid air round g, a small amount of chlorine was admitted to the apparatus. This was allowed to distil over into d and the liquid air bath was replaced around g. After about one minute most of the HCl present had distilled back to f, and the connecting tube was at once sealed off at the capillary h. The methylcyclohexane bath was replaced by liquid air, and traces of permanent gas were removed by pumping until the Pirani reading was again v_0.

(3) The section of apparatus between traps k and l was filled with hydrogen, the tube f being heated and the charcoal trap e surrounded by liquid air.

After a few hours the purified hydrogen was let into the reaction vessel and then pumped out until the pressure could be measured on the Pirani gauge. The hydrogen capillary, i, was sealed off.

(4) The apparatus was now ready for measurement of the reaction. The light source was a 100 watt filament lamp placed 3 cm. from one end of the insolation vessel.   After taking the steady reading the gauge current was switched off and the liquid air bath round d replaced by a bath at the desired constant temperature.   Ten minutes' interval was allowed for equilibration, and the insolation then started.   Afterwards liquid air was put round d and the steady gauge reading taken.

Three baths were used.   The temperature of each bath was taken from the International Critical Tables,[5] and the vapour pressures corresponding to each temperature were obtained from the data of Harteck,[6] the most recent known to us.   Details of these baths are summarised in Table I., where column I gives the nature of the bath, II the absolute temperature, and III the chlorine pressure at this temperature.

TABLE I.

	I.	II.	III.
Melting carbon disulphide .		161·4° K.	1·7 mm.
„ methylcyclohexane .		146·6° K.	0·11 mm.
„ allyl chloride . .		136·6° K.	0·012 mm.

Results.

The first two experiments were really only preliminary : they served to show that the gas mixture prepared in the manner indicated was reactive at moderately high pressures, and that the Pirani gauge was quite reliable in presence of chlorine.   The zero reading after an experiment was the same as before, so that no corrosion of the filament could have occurred.

The results of experiments 3 and 4 are collected in Tables II. and III.

TABLE II.

(Pirani zero = 3·50 volts.   Refrigerant : melting methylcyclohexane.)

TABLE III.

(Pirani zero = 3·69 volts.   Refrigerant : melting methylcyclohexane.)

Time (minutes).	v (volts).	p_{H_2} (in mm.).	Time (minutes).	v (volts).	p_{H_2} (in mm.).
0	14·20	0·419	0	13·68	0·347
40	13·50	0·378	87	13·56	0·340
81	13·05	0·351	269	13·29	0·325
121	13·10	0·355	362	13·19	0·321
241	12·62	0·327	459	13·04	0·313
317	12·00	0·292	511	13·00	0·310
379	11·53	0·268	606	13·00	0·310
455	11·00	0·241	686	12·89	0·305
520	10·89	0·236			
597	10·39	0·212			

[5] International Critical Tables, 1, 176, 182, 214.
[6] Harteck, *Z. physik. Chem.*, 134, 21, 1928.

Although the reaction rate appears to vary rather irregularly in these experiments, there can be no doubt that a definite reaction was occurring. The irregularity was found to be due to the varying length of tube d immersed in liquid air while readings were being taken, and in the fifth experiment, summarised in Table IV., this length was kept constant. It should also be mentioned that there was a certain slow corrosion of the gauge supports during the course of these experiments, and although the tungsten filament itself seemed to be unharmed it was possible that the results obtained might be connected with this change. In the fifth experiment, therefore, we used a special platinum gauge constructed by the General Electric Company. The gauge constant, α, was 0·035.

TABLE IV.

Platinum gauge.   Zero reading 4·13 volts.

Time (minutes).	v (volts).	p_{H_2} (in mm.).	p_{Cl_2} (in mm.).	Time (minutes).	v (volts).	p_{H_2} (in mm.).	p_{Cl_2} (in mm.).
0	9·55	0·152	0·11	0	7·92	0·0936	0·012
60	9·47	0·148		184	7·84	0·0910	
122	9·33	0·1435		365	7·79	0·0896	
199	9·20	0·1383		563	7·75	0·0882	
271	9·09	0·1343					
345	8·91	0·1277		0	7·69	0·0864	1·7
401	8·81	0·1240		60	7·50	0·0805	
457	8·705	0·1206		127	7·31	0·0749	
				192	7·14	0·0694	
0	8·705	0·1206	0·012				
85	8·67	0·1190		0	7·195	0·0711	1·7
161	8·67	0·1190		62	7·050	0·0670	
382	8·58	0·1160		122	6·875	0·0620	
580	8·49	0·1127		201	6·675	0·0564	
				271	6·495	0·0514	
0	8·49	0·1127	0·11				
61	8·405	0·1100		0	6·495	0·0514	0·11
124	8·30	0·1064		60	6·450	0·0504	
198	8·18	0·1022		130	6·375	0·0483	
264	8·06	0·098		199	6·300	0·0464	
325	8·00	0·0962		241	6·255	0·0452	
384	7·91	0·0952					

Discussion.

We consider that the combination of hydrogen and chlorine at chlorine pressures much below 0·2 mm. is definitely proved by the experiments described in this paper. There is a faint possibility that Harteck's vapour pressures are too low (compare Henglein, Rosenberg and Muchlinski[7]), and hence that the chlorine pressure at 146·6° K. is considerably greater than 0·11 mm., but the experiment with the melting allyl chloride bath seems to be quite free from ambiguity. It is hoped that one of us (H. C. C.) will shortly be able to measure accurately the vapour pressures of solid chlorine in continuation of this work. Quantitative experiments on the reaction of hydrogen and chlorine at low pressures are also in progress.

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[7] Henglein, Rosenberg and Muchlinski, Z. Physik, **11**, 1, 1922.

Summary.

1. The Pirani gauge has been used in following the reaction between hydrogen and chlorine at low constant chlorine pressures.

2. Under the conditions of these experiments, it is shown that hydrogen and chlorine react at chlorine pressures below 0·2 mm., and hydrogen pressures at least down to 0·04 mm.

3. This result, in agreement with Marshall's work, is directly opposed to that of Trifonoff.

GENERAL DISCUSSION.

Professor Allmand (*London*) said : The purpose of the experiments of Bateman and Craggs was merely to test the truth of the remarkable conclusion come to by Trifonoff and Semenoff, and, as the work is being continued in various directions, their paper contains no quantitative analysis of their experimental results. Professor Bodenstein has, however, drawn attention to the fact that oxygen retardation in the $H_2 - Cl_2$ reaction necessitates three-fold collisions and that, assuming the correctness of the Thon mechanism, this leads to the conclusion that the reaction rate must be retarded by an increase in total pressure. In this connection, a closer analysis of the results of Bateman and Craggs is perhaps of interest. If the data in their Table IV. are plotted in the form of log p_{H_2} against time, straight lines are obtained, of slope characteristic of the prevailing chlorine pressure, and representing the effect of the latter on the kinetics of the reaction. Expressed on an arbitrary scale, the results are as follows :—

p_{Cl_2} in mm. . . .	1·7	0·11	0·012
Slope of curve . .	50·5	21·8	5·2

It is clear that, at all events in these particular experiments, the rate of reaction increases less rapidly than the chlorine pressure. This suggests a formula of the type (omitting all constants) :

$$\text{Rate} \propto \frac{I_0[H_2][Cl_2]^2}{[M][O_2]([Cl_2] + [H_2])},$$

and it is interesting to recall that Chapman and his collaborators have always asserted in recent years that hydrogen exerts a retarding influence on the reaction. I agree that such an interpretation of the results of Bateman and Craggs involves the assumption that they were using gas mixtures relatively rich in oxygen.

THE PHOTOSENSITISED DECOMPOSISION OF NITROGEN TRICHLORIDE AND THE INDUCTION PERIOD OF THE HYDROGEN-CHLORINE REACTION.

BY J. G. A. GRIFFITHS AND R. G. W. NORRISH.

The study of gaseous reactions photosensitised by chlorine has led to a number of interesting discoveries in the past which have often been of assistance in elucidating the mechanism of associated photochemical reactions. For example we have the photosensitised formation of carbon dioxide in the phosgene synthesis, and of water in the hydrogen chlorine reaction, when oxygen is present, while perhaps the simplest example known at the present time is the photosensitised decomposition of ozone. Now to these reactions is added another example, the photosensitised decomposition of nitrogen trichloride by chlorine, which forms the subject of the present memoir.

It is well known that artificial induction periods can be produced in mixtures of pure hydrogen and chlorine by the addition of small quantities of ammonia and other substances [1] and in continuation of this work, with an apparatus consisting essentially of a dry reaction vessel at constant temperature attached to a Bourdon gauge sensitive to $0 \cdot 002$ mm. of Hg, we have found that a small but clearly marked and repeatable rise of pressure is obtained during the period of inhibition produced by the ammonia.[2] The effect is quite distinct from the Budde effect or instantaneous increase of pressure which occurs when the chlorine is first illuminated, and from the Draper effect which marks the termination of the induction period and the sudden onset of the rapid hydrogen-chlorine reaction. The type of curve obtained is shown in Fig. 1.

When a large excess of chlorine is added rapidly to ammonia, a fine cloud of ammonium chloride is formed, and, if the pressure of the ammonia is not too great (< 25 mm. Hg) nitrogen trichloride is also produced. The equations are as follows :—

FIG. 1.

$$4 \ NH_3 + 3 \ Cl_2 = 3 \ NH_4Cl + NCl_3$$
Nitrogen trichloride formed.

$$8 \ NH_3 + 6 \ Cl_2 = 6 \ NH_4Cl + N_2 + 3 \ Cl_2$$
No nitrogen trichloride formed.
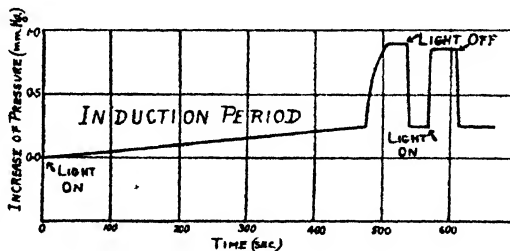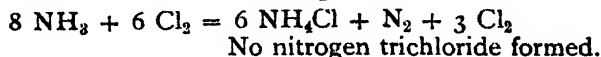
[1] Burgess and Chapman, *J. Chem. Soc.*, **89**, 1399, 1906; Chapman and McMahon, *ibid.*, **95**, 1717, 1909; **97**, 847, 1910; Norrish, *ibid.*, **127**, 2323, 1925.
[2] Griffiths and Norrish, *Proc. Roy. Soc.*, A, **130**, 591, 1931; *Nature*, **127**, 14, 1931.

It is found that if the cloud of ammonium chloride is first allowed to settle out on the walls of the mixing vessel, and the residual chlorine added to hydrogen in a separate reaction vessel, the resulting mixture is subject or not to an induction period, according as nitrogen trichloride has or has not been formed by the above reactions.

By these and other experiments (Griffiths and Norrish [2]) it was proved that nitrogen trichloride is solely responsible for the induction period produced by the introduction of ammonia, in full accordance with the views of Chapman and co-workers.[1]

Characteristics of the Reaction.

The gradual increase of pressure during the induction period has been traced to the photosensitive decomposition of the nitrogen trichloride by the chlorine, in accordance with the net reaction *

$$2\ NCl_3 \rightarrow N_2 + 3Cl_2.$$
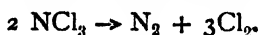
It is found that *exactly similar increases of pressure are obtained when the hydrogen is omitted from the mixture*, and the rate of reaction is always proportional to the quantity of light absorbed by the chlorine. Examples of the decomposition curves obtained with homogeneous light of wavelength $365\mu\mu$ are shown in Fig. 2. Similar curves are obtained with light
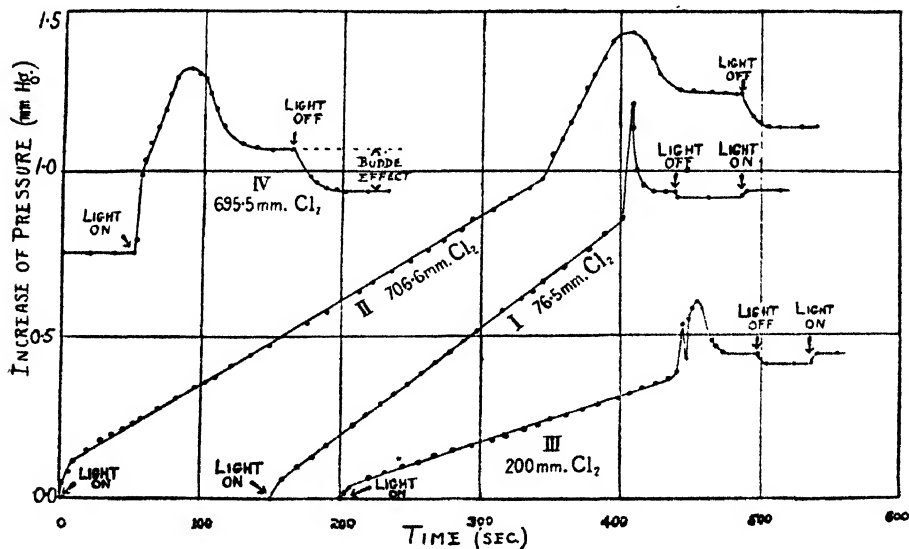
FIG. 2.

of wave-length $436\mu\mu$ and also with the full radiation of the mercury lamp. It will be seen that they are strictly of zero molecular order, and that the termination of the reaction is signalised by a rapid change of pressure.

This pressure leap is one of the most puzzling features of the reaction; its sharpness was at first found to be decreased by increase of chlorine pressure, but this has been subsequently shown to be connected with a diffusion effect, arising from the fact that only the central part of the

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* Bowen (*J. Chem. Soc.*, **123**, 1199, 1923) also records that the photo-decomposition of nitrogen trichloride in carbon tetrachloride is in accordance with this equation.

contents of the reaction vessel were illuminated by the light beam. When the light beam is made to fill the whole vessel, the pressure change is just as sharp at high pressures as at low. This fact definitely seems to fix the seat of reaction in the gas phase and rules out the possibility of accounting for the zero order of the reaction by a surface mechanism. In confirmation of this, it has been found—firstly by using reaction bulbs of different size, and secondly by using a reaction vessel containing a number of movable transparent vanes—that variation of (a) the total surface, and (b) the total illuminated surface, has nothing but a very secondary effect upon the course of the reaction.

The Quantum Efficiency.

When the intensity of the light is measured it is found that the quantum efficiency of the decomposition of the nitrogen trichloride is very dependent on the chlorine pressure. At low pressures of chlorine it may rise to values as high as 17, while as the chlorine pressure is increased it falls rapidly to a limiting value of about 2, as is shown in the curve in Fig. 3. It will be seen that the points for decomposition with homogeneous blue light (436$\mu\mu$), and ultra-violet light (365$\mu\mu$) fall equally well on the curve, and show that the photochemical effect of these two wave-lengths is identical. If, however, longer wave-lengths (570, 546$\mu\mu$) are used, no decomposition is observed. These results are made clearer when the quantum efficiency is plotted against the reciprocal of the chlorine pressure as in Fig. 4. From the straight line obtained it will be seen that the results can be represented by the empirical equation
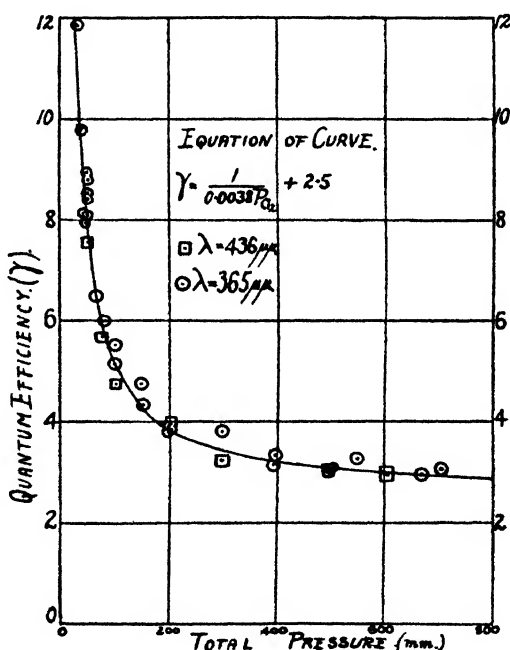
FIG. 3.

$$\gamma = \frac{1}{kP_{Cl_2}} + 2\cdot5,$$

where γ is the quantum efficiency, $\frac{1}{k}$ is the slope of the curve, and 2·5 the intercept on the axis of γ. That this equation satisfactorily represents the results will be apparent from the conformity of the experimental points to the curve in Fig. 3, which is accurately drawn from the above equation, in which k is assigned the value 0·0038.

The Effect of Inert Gases.

It is clear, in view of the high values of the quantum efficiency at low pressures, that we must have some type of chain mechanism operating in the decomposition, and it therefore became of interest to investigate how far the depression of the quantum efficiency — i.e. a shortening of chain length — at high pressures was attributable to some effect specific to the chlorine alone, or whether to some effect common to other gases.

FIG. 4.
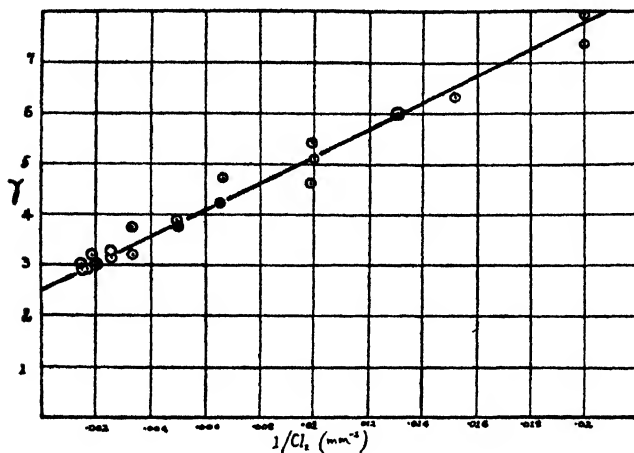
This point was tested by measuring the quantum efficiency, γ, in the presence of foreign gases, and it has been established that other gases act similarly to the chlorine in depressing the value of γ. For example, in Fig. 5 are shown the results obtained in the presence of helium and carbon dioxide. Similar curves were obtained with argon, nitrogen, and oxygen. They represent the effect on the quantum efficiency of increasing the pressure of the foreign gas when the pressure of chlorine is kept constant, and are all reproduced by equations of the type—

$$\gamma = \frac{1}{0.0038 P_{Cl_2} + k_x P_x} + 2.5,$$

where k_x and P_x refer to the added gas, and the constant for the chlorine is the same in all cases. The curves in the figure represent the accurate plots of the above empirical equation in which has been

FIG. 5.

inserted the appropriate values of k_x, and the degree of conformity of the observed results can be gathered from the distribution of the experimental points about the lines. The values obtained for k_x are as follow :—

k_x
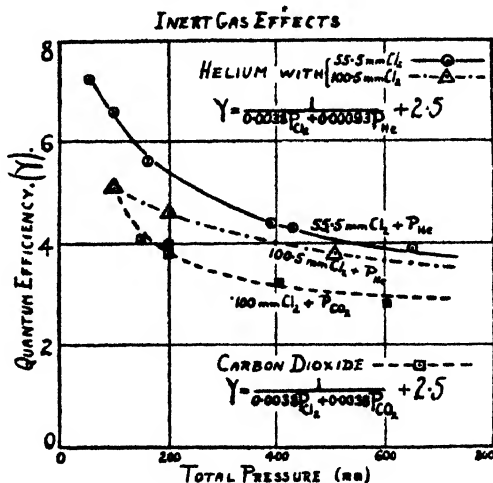
Helium	.	.	.	.	.	0·00093
Argon	.	.	.	.	.	0·0016
Nitrogen	.	.	.	.	.	0·0017
Oxygen	.	.	.	.	.	0·0025
Carbon dioxide	.	.	.	.	0·0038
Chlorine	.	.	.	.	.	0·0038

These constants represent the relative effectiveness of these gases in depressing the quantum efficiency to the constant final value of 2·5 at high pressures. The relative effectiveness of these gases is in the same order as that of their effects in the photochemical decomposition of ozone[3] in catalysing the recombination of bromine atoms,[4] and approximately in the quenching of fluorescence of such substances as mercury,[5] sodium,[6] iodine,[7] and nitrogen peroxide.[8]

This relationship is of some importance and suggests that the gases exercise their effect in the present reaction through the medium of collision in the gas phase, possibly in the stabilisation of some intermediate product which brings about the termination of the reaction chain. This point will be referred to later. It is of interest to note that chlorine acts both as a positive and negative catalyst by virtue of its double rôle of photosensitiser and inhibitor.

The Mechanism.

The facts so far recorded indicate that we are concerned with a homogeneous gas reaction photosensitised by chlorine. The reaction proceeds by chains of short length which are shortened by increase of pressure, either by the addition of chlorine, or foreign gases. The rate of decomposition is directly proportional to the light absorbed by the chlorine.

In searching for a mechanism of the reaction we may first proceed in a perfectly non-committal way with the aid of the concept of the reaction centre. A reaction chain passes through a series of recurrent phases, but at any moment is represented by some atom or active complex which carries on the mechanism. We may, therefore, speak of the concentration, n, of reaction centres. We shall assume that the rate of decomposition of nitrogen trichloride is at any moment proportional to the number of collisions it makes with such centres, then,

$$- \frac{d(\text{NCl}_3)}{dt} = k' . n . [\text{NCl}_3]. \qquad . \qquad . \qquad . \qquad (i)$$

In conformity with the fact that the reaction is of zero order over nearly the whole of its course, and proceeds at a speed proportional to the light absorbed ($L_{abs.}$) by the chlorine, it follows that

$$n \propto \frac{L_{abs.}}{[\text{NCl}_3]}.$$

[3] Kistiakowsky, Z. physikal. Chem., 117, 337, 1925.
[4] Jost and Jung, ibid., B3, 83, 1929.
[5] Stuart, Z. Physik, 32, 262, 1925.
[6] Mannkopff, ibid., 36, 315, 1926.
[7] Wood and Franck, Phil. Mag., 21, 309, 314, 1911.
[8] Baxter, J. Amer. Chem Soc., 52, 3920, 1930.

This relationship is obtained if we suppose that the chains are generated by the photochemical dissociation of the chlorine molecule, and destroyed by some act in which the nitrogen trichloride participates. Since, in addition, the rate of decomposition of nitrogen trichloride is inversely proportional to the partial pressures of the other gases in the system the number of reaction centres must also be governed by the concentration of these substances. This result is obtained if the termination of the chains be conditioned by a three body collision. We shall therefore write

$$\frac{dn}{dt} = k_1 L_{abs.} \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \text{(ii)}$$

$$-\frac{dn}{dt} = n[\text{NCl}_3](k_2 P_2 + k_3 P_3 + \quad) \qquad \cdot \qquad \cdot \qquad \text{(iii)}$$

where P_2, P_3, etc., represent the partial pressures of the various gases in the system and k_2, k_3, etc., are specific constants. We thus obtain for the number of reaction centres at any moment

$$n = \frac{k_1 L_{abs.}}{[\text{NCl}_3](k_2 P_2 + k_3 P_3 + \quad)}. \qquad \cdot \qquad \cdot \qquad \text{(iv)}$$

It therefore follows that the reaction between a nitrogen trichloride molecule is differently determined according as the collision is of a binary or a ternary character; in the former case the chain is propagated, in the latter it is terminated. Since, however, nitrogen trichloride reacts in any case, and is therefore destroyed, the expression for its rate of decomposition will contain two terms representing respectively these two possibilities. It therefore follows that

$$-\frac{d(\text{NCl}_3)}{dt} = k' \cdot n \cdot [\text{NCl}_3] + n[\text{NCl}_3](k_2 P_2 + k_3 P_3 + \quad) \cdot \quad \text{(v)}$$

substituting for n in equation (v), we obtain

$$-\frac{d(\text{NCl}_3)}{dt} = \frac{k' k_1 L_{abs.}}{(k_2 P_2 + k_3 P_3 + \quad)} + k_1 L_{abs.} \qquad \cdot \qquad \text{(vi)}$$

If $[\text{NCl}_3]$ is measured in molecules, and $L_{abs.}$ in quanta per second, then the quantum efficiency γ is given by

$$\gamma = -\frac{1}{L_{abs.}} \frac{d[\text{NCl}_3]}{dt}. \qquad \cdot \qquad \cdot \qquad \cdot \qquad \text{(vii)}$$

Further, since each quantum absorbed generates two chlorine atoms and therefore two reaction centres,

$$\frac{dn}{dt} = 2 L_{abs.} \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \text{(viii)}$$

and, see equation (ii), $k_1 = 2$. Hence substituting for $L_{abs.}$ (equation (vii)) in equation (vi)

$$\gamma = \frac{2k'}{(k_2 P_2 + k_3 P_3 + \ldots)} + 2. \qquad \cdot \qquad \cdot \qquad \text{(ix)}$$

This equation therefore agrees closely with the experimentally determined result

$$\gamma = \frac{1}{k P_{\text{Cl}_2} + k_x P_x} + 2 \cdot 5.$$

It is thus clear that we can theoretically describe the course of the reaction on the basis of reaction chains which have their inception from

chlorine atoms formed by the light in the gas phase, and their conclusion through some ternary collision in which both nitrogen trichloride and a third body participate.

Nature of the Reaction Chains.

As to the nature of the chain mechanism, little would appear to be gained at the present stage by undue speculation, but the question has some interest in view of the very few possibilities which exist in this simple system.   We may enquire what would be the fate of chlorine atoms liberated in an environment of nitrogen trichloride molecules.   The reaction

$$NCl_3 + Cl = N + 2Cl_2$$
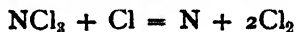
is not possible in view of energy considerations,[9] and we find that we are limited to a choice of two mechanisms, (a) and (b), which may be represented as follows :

$$
\begin{aligned}
NCl_3 + Cl &= NCl_2 + Cl_2 & \quad (1) \\
NCl_2 + NCl_3 &= N_2 + 2Cl_2 + Cl & \quad (2)
\end{aligned} \Biggr\} (a)
$$

$$
\begin{aligned}
NCl_3 + Cl &= NCl + Cl_3 & \quad (1) \\
NCl_3 + Cl_3 &= NCl + 2Cl_2 + Cl & \quad (2) \\
NCl + NCl &= N_2 + Cl_2 . & \quad (3)
\end{aligned} \Biggr\} (b)
$$
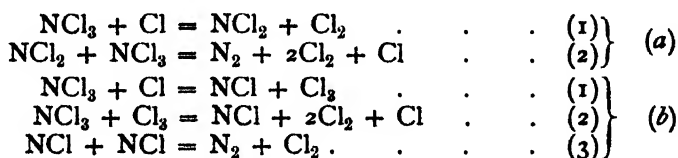
Reactions (1) and (2) in these schemes repeat themselves and so propagate the reaction indefinitely.   For the termination of the chain reactions, it is a kinetic necessity that there should occur a ternary collision in which NCl_3, a reaction centre and a third body participate.

On examination of the various possibilities we have been led to the view that the only ternary encounter conforming to these requirements is represented by the equation

$$NCl_3 + Cl + X = NCl_4 + X.$$

In this instance the effect of the third body in stabilising the NCl_4 is fully in conformity with experience in other reactions.

No final choice between mechanisms (a) and (b) can be made unless one of the intermediate products can be isolated, and in this we have so far not succeeded, a fact which is not surprising in view of their undoubted short life.   We may, however, temporarily prefer scheme (a) to scheme (b) in view of the fact that it involves the postulation of only one intermediate compound – NCl_2 – as against two, NCl and Cl_3, in scheme (b).

The complete mechanism is then

$$
\begin{aligned}
Cl_2 + h\nu &= Cl + Cl & \quad (1) \\
NCl_3 + Cl &= NCl_2 + Cl_2 & \quad (2) \\
NCl_2 + NCl_3 &= N_2 + Cl_2 + Cl_2 + Cl & \quad (3) \\
NCl_3 + Cl + X &= NCl_4 + X & \quad (4) \\
NCl_4 + NCl_4 &= N_2 + 4Cl_2 & \quad (5)
\end{aligned}
$$
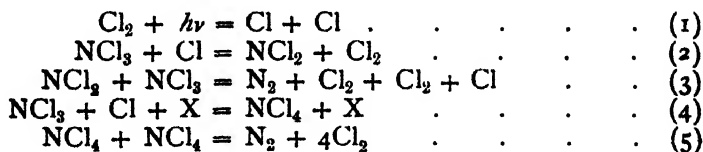
The full kinetics of the reaction are adequately described by this scheme ; a most significant point is the high efficiency of the ternary reaction (4) as compared with the binary reaction (2) as expressed by the powerful effect of increase of total pressure in depressing the chain length to the limiting value of about 2.

[9] Noyes and Tuley, *J. Amer. Chem. Soc.*, **47**, 1336, 1925; Birge, *Trans. Faraday Soc.*, **25**, 706, 1924.

The Induction Period of the Hydrogen-Chlorine Reaction.

The bearing of these results on the mechanism of the inhibiting action of nitrogen trichloride (derived from ammonia), on the hydrogen chlorine reaction, may now be discussed. It has been found that the duration of the induction period is coincident with the time required to destroy the nitrogen trichloride in the system. In this process the hydrogen acts as a foreign gas exactly in the same way as those studied above, the constant for the inhibiting action being $k_{H_2} = 0.00093$—identical with that of helium. Further, preliminary experiments indicate that during the induction period, hydrogen chloride is being formed at a rate comparable with the rate of decomposition of nitrogen trichloride.[10] It would thus appear that the hydrogen-chlorine chains must be shortened some thousand-fold, and this must be effected by the action of nitrogen trichloride on the chlorine atoms, and not on the hydrogen atoms, since as shown above, hydrogen does not act otherwise than as an inert diluent. There are two ways in which nitrogen trichloride might decrease the concentration of chlorine atoms propagating the hydrogen-chlorine chain. One is by virtue of the exceptionally high efficiency of process (4) above, a point to which we have already drawn attention, especially since the reaction $Cl + H_2 = HCl + H$ is relatively inefficient.[11] The second is in view of the possibility that it is only excited chlorine atoms which give rise to the chains in the hydrogen chlorine reaction [12] a view which receives support from the work of Rollefson.[13] If these excited chlorine atoms were replaced by inactive chlorine atoms as soon as they participated in the nitrogen trichloride chain, we should obtain the very drastic lowering of the quantum efficiency of hydrogen chloride formation observed. Whether either or both of these two mechanisms are operative, we hope to establish by further experiment.

Summary.

A general account of the kinetics of the newly discovered photosensitised decomposition of nitrogen trichloride is given, and its bearing on the mechanism of the induction period of the hydrogen-chlorine reaction is discussed.

[10] Compare also Bunsen and Roscoe, *Phil. Trans.*, 147, 355, 381, 1857; Burgess and Chapman.[1]
[11] Kistiakowsky, *J. Amer. Chem. Soc.*, 52, 1868, 1930.
[12] Cremer, *Z. physikal. Chem.*, 128, 285, 1927.
[13] *J. Amer. Chem. Soc.*, 51, 770, 1929.

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GENERAL DISCUSSION.

Professor M. Bodenstein (*Berlin*) said : The explosion-like sudden increase of pressure at the moment when the last traces of NCl_3 disappear calls to mind an analogous observation made by Beaver and Stieger [1] in connection with the decomposition of Cl_2O and by Schumacher and Stieger [2] with that of ClO_2.

[1] Beaver and Stieger.   [2] Schumacher and Stieger.

In both these cases the slow decomposition is followed by a real explosion at the moment when some 30 mm. Hg of the reactant gas are still present. This explosion can be avoided if fresh Cl_2O is added just before it is due to occur. If this fresh Cl_2O is nearly consumed, then, of course, the explosion happens again.

Though the mechanism of these reactions is not yet cleared up in detail, we may assume that in the smooth part there is a reaction between an intermediate product and the initial substance during which the concentration of the former grows greater and greater. The explosion then is thought to be a reaction between the molecules of the intermediate products.

Professor Allmand (*London*) said: The rapid rise in pressure found by Griffiths and Norrish just before the end of their reaction is very similar to what was noticed (*a*) by Lewis and Schumacher in their work on the thermal reaction between bromine and ozone, and (*b*) by Weigert in the photo-decomposition of chlorine-ozone mixtures. In the former case, the result is visibly due to the decomposition into gaseous products of a deposit which has formed on the vessel walls. Dr. J. W. T. Spinks has worked recently on the latter reaction at King's College. There is evidence that the vessel walls play an appreciable part in this case, and in particular, we have concluded that the final pressure rise is due to Cl atoms, which can find no more O_3 molecules in the gas phase with which to react, reaching the vessel walls and there catalysing the decomposition of adsorbed ClO_3 or Cl_2O_6 to gaseous Cl_2 and O_2. The effects produced are of the order one would expect with an adsorbed layer of one or a few molecules thick.

Is a similar interpretation of the end pressure rise at all possible in the experiments of Griffiths and Norrish, *e.g.* decomposition of an adsorbed NCl_3 layer? It would seem that the effects of varying the Cl_2 pressure and the fraction of cell volume illuminated would be qualitatively similar with either mechanism, as diffusion processes (NCl_3 molecules into the light beam or Cl atoms out of the light beam) are involved in both cases.

Professor J. Eggert (*Leipzig*) said: I would ask whether in the photo-chemical decomposition of nitrogen chloride, perhaps at higher pressures or in the liquid phase of the substance, an explosion would take place. The literature mentions such a result, but I have never noticed in the case of solid nitrogen iodide (NI_3NH_3), in spite of the employment of very great intensity of light, any photochemical explosion such as occurs in the case of hydrogen chlorine mixtures.

Dr. R. G. W. Norrish (*Cambridge*), in reply, said: Professor Allmand raises the question of the possibility of the photo-decomposition of the nitrogen trichloride being a surface decomposition; this was a view to which we gave very careful consideration in the first instance on account of the peculiar kinetics, and it is one which in our opinion cannot be upheld. I would emphasise that as stated in our paper we used vessels cf different sizes in which the ratio of surface to volume was widely varied and in addition the illuminated surface was also varied by using a vessel with movable vanes. No dependence of the quantum efficiency on surface was observed. Besides this, the inert gas effect is not understandable in terms of a surface reaction, while it is readily explainable in terms of a reaction in the gas phase. No heterogeneity was observed by the use of the Tyndall beam. If it is Professor Allmand's suggestion that the explosive effect *only* is associated with the surface, and that it is due to the sudden decomposition of a film of adsorbed nitrogen trichloride by chlorine atoms which finally diffuse there only when the gas reaction is complete, I am still in disagreement. Firstly the permanent increase of pressure

resulting from the explosive effect is of the order o·1 mm., a magnitude too great to be accounted for by the decomposition of a surface film. Secondly, the greater part of the explosive effect is obviously thermal in origin, since the maximum explosive pressure change is always large compared with the permanent pressure charge. It thus evidently has its origin in the heat effect of some very rapid reaction which sets in at the end of the change. If this had its seat on the surface there would be no thermal effect observable on the body of the gas as the heat would be conducted away by the glass wall and would never enter the gas at all. It thus seems clear that the explosive effect is essentially located in the gas phase. I am very interested to hear of the analogous effects in Cl_2O and ClO_2 mentioned by Professor Bodenstein. It would appear that in these cases too we have very similar effects which will probably be eventually explained along similar lines to those by which we seek to explain the present effect.

Perhaps I may be permitted briefly to indicate these. On refering to our paper (equation 1) you will see that throughout the main course of the reaction the product n (NCl_3) remains constant, in agreement with the fact that the reaction is of zero order. We have assumed that the intermediate substance whose concentration is represented by n is alternately represented by NH_2 and Cl in the chain mechanism, although its exact nature is immaterial to our present argument. It follows that as the concentration of NCl_3 falls off (curve I) that of the intermediate product (n) will grow with steadily increasing speed (curve II) and in the last stages of the reaction its concentration will momentarily mount up to a comparatively very high value, the product n(NCl_3) always remaining constant. When the magnitude of n becomes appreciable and (NCl_3) small, the previously normal reaction between intermediate and nitrogen trichloride no longer predominates, and the intermediate now becomes subject to some other process of removal such as reaction with itself. This constitutes the rapid reaction, the thermal effect of which we have called the explosive reaction. We might suggest
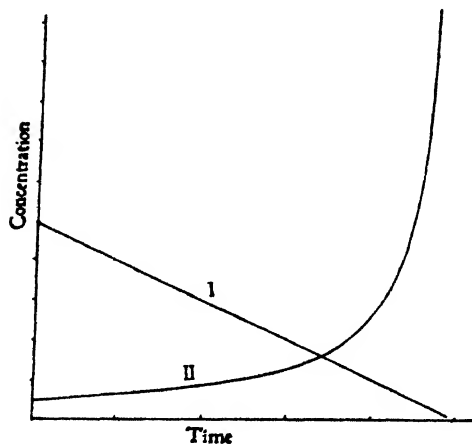
$$Cl + Cl + X = Cl_2 + X'$$
$$NCl_2 + NCl_2 = N_2 + 2Cl_2$$
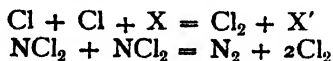
both of which could only take place after practically all the NCl_3 has gone, and both of which are strongly exothermic.

Alternatively it may be that the concentration of the intermediate finally reaches an explosive limit beyond which it is suddenly decomposed according to the well-known kinetics of explosion reactions.

With reference to Professor Eggert's question we have not dealt with nitrogen trichloride at high pressures or in the liquid condition, and I am afraid I am not able to give an answer. I do not even know how far pure nitrogen trichloride is of itself light sensitive, as it is very doubtful if any experiments have ever been done completely in the absence of the photo-

sensitive effect of chlorine. It does, however, seem highly probable that in the liquid condition a "thermal" explosion of nitrogen trichloride might be stimulated by light.

THE PHOTOSENSITISED FORMATION OF HYDROGEN PEROXIDE IN THE SYSTEM HYDROGEN-OXYGEN CHLORINE.

BY R. G. W. NORRISH (*Cambridge*).

Received 24th March, 1931.

The part played by oxygen in reducing the speed of the photochemical reaction between hydrogen and chlorine has been interpreted in various ways. The general kinetics of the reaction indicate that (when oxygen is present) the velocity is approximately inversely proportional to the pressure of oxygen, and it may be deduced that practically all the reaction chains are terminated through the agency of an oxygen molecule. On the basis of the "energy chain" mechanism supported by earlier workers[1] this action was supposed to consist in a deactivation of the energy-rich chlorine or hydrogen chloride molecules by collisions of the second kind

$$Cl_2^* + O_2 = Cl_2 + O_2^*$$
$$HCl^* + O_2 = HCl + O_2^*$$
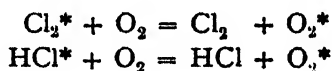
but the explanation suffers from the disadvantage that oxygen has practically no effect on the somewhat analogous photo-synthesis of phosgene. We shall not pursue it further since for other well-known reasons, both spectroscopic and kinetic[2] it may be held that the "energy chain" must now be replaced by a mechanism involving propagation by chlorine and hydrogen atoms, after the scheme first suggested by Nernst.[3] In this, the primary act of the light is to dissociate the chlorine molecule into atoms

$$Cl_2 = Cl + Cl'$$

of which one atom is in the metastable $2P_1$ state.[4] A feature of the later views of this mechanism is that the chain is only propagated by the excited chlorine atom, which alone is deemed able to dissociate the hydrogen molecule

$$Cl' + H_2 = HCl + H.$$

The reaction chain is then continued by

$$H + Cl_2 = HCl + Cl'$$
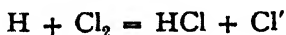
and these phases are repeated indefinitely.

[1] Bodenstein, *Z. Electrochem.*, **22**, 58, 1916; Chapman, *J.C.S.*, **123**, 3079, 1923; Thon, *Fortschr. Chem.*, **18**, Heft 11, 1926.
[2] Franck, *Trans. Farad. Soc.*, **21**, 536, 1926; Kuhn, *Z. Physik*, **39**, 77, 1927; Rollefson, *J. Amer. Chem. Soc.*, **51**, 770, 1929.
[3] Nernst, *Z. Electrochem.*, **22**, 62, 1916.
[4] Kuhn, *loc. cit.*, 2.

According to Cremer,[5] the effect of oxygen in reducing the speed is explained by its deactivating effect on the excited chlorine atoms,

$$Cl' + O_2 = Cl + O_2'$$

which are thereby rendered incapable of reacting with hydrogen. It is known that the oxygen simultaneously reacts to form water,[6] and this has been represented as a reaction between the excited oxygen molecules produced as above, and hydrogen molecules according to the equation proposed by Cremer

$$O_2' + 2H_2 = 2H_2O.$$
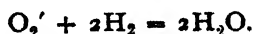
Quite apart from kinetic difficulties, it would seem, however, very doubtful whether this mechanism can be admitted, since the low energy of activation of the metastable chlorine atom (0·109 volt), is certainly insufficient to activate the oxygen molecule to the point of reaction with hydrogen.

Further, any chemical process involving the removal of chlorine atoms by reaction with oxygen to form for example ClO_2 suffers from the difficulty, among others, that it should involve a similar retardation of the phosgene synthesis, by oxygen, which as already stated is not observed, nor has any such oxygenated product of chlorine ever been observed. We shall therefore propose that oxygen acts, not by deactivation of or reaction with chlorine atoms, *but solely by reaction with the hydrogen atoms propagating the reaction chains.*

The matter is now made much clearer by the work of Haber and his school[7] on the homogeneous reaction between hydrogen and oxygen. They give strong evidence, based upon a spectroscopic study of the hydrogen-oxygen flame, that the reaction is propagated by chains involving free hydroxyl radicles, according to the scheme

$$H + H_2 + O_2 = HO + H_2O \qquad . \qquad . \qquad . \quad (a)$$
$$HO + H_2 = H + H_2O. \qquad . \qquad . \qquad . \quad (b)$$
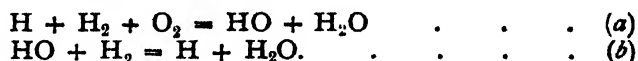
Below 400° C. which is the lowest temperature of explosion, reaction (*b*) requires activation and cannot proceed spontaneously, so that the chain mechanism can no longer occur. Instead, the free hydroxyl radicles may unite to form hydrogen peroxide and this can be isolated,—for example by playing the flame on a cold surface such as solid carbon dioxide.

These results would seem to give us the key to the action of oxygen in the hydrogen chlorine reaction. The free hydrogen atoms propagating the hydrogen-chlorine chains will also react according to equation (*a*) above; but since reaction (*b*) cannot follow at ordinary temperatures there should be an accumulation of hydrogen peroxide in the system. In confirmation of this view we may cite the experiments of Marshall[8] in which hydrogen peroxide in considerable quantities was produced in mixtures of hydrogen and oxygen by the photosensitising action of mercury vapour in light of wavelength 2536 ÅU. In this case, there is little doubt that the first phase of the reaction is the liberation of hydrogen atoms, and quantitative evidence for the scheme

[5] Cremer, *Z. physikal. Chem.*, **128**, 285, 1927.
[6] Weigert, *Ann. Physik*, **24**, 243, 1907; Norrish and Rideal, *J.C.S.*, **127**, 790, 1925; Cremer, *loc. cit.*, 5.
[7] Bonhoeffer and Haber, *Z. physikal. Chem.*, A **137**, 263, 1928; Farkas, Haber and Harteck, *Naturw.*, **19**, 266, 1930.
[8] Marshall, *J. Amer. Chem. Soc.*, **49**, 2763, 1927.

$$Hg^* + H_2 = H + H + Hg$$
$$H + O_2 + H_2 = HO + H_2O$$
$$HO + HO + M = H_2O_2$$
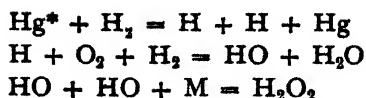
has recently been adduced by Klinkhardt and Frankenburger.[9]

It therefore seemed probable that hydrogen peroxide as well as water is also a product in the hydrogen-chlorine reaction when oxygen is present, and this has been tested and fully confirmed in the following experiments.

Experimental.

(*a*) Hydrogen (250 mm.), oxygen (250 mm.), and chlorine (150 mm.) were enclosed in a spherical reaction vessel of about 250 c.c. capacity. Attached to the reaction vessel was a side tube with a stopcock through which a small quantity (5 c.c.) of water could be rapidly introduced. The reaction vessel was attached to a glass Bourdon gauge sensitive to small pressure changes of 0·002 mm., and kept at a constant temperature by immersion in a bath of water. The vessel and contents were irradiated for 80 minutes by a mercury vapour lamp, using glass lenses so that no light of wavelength less than 3500 ÅU entered the system. During this time the pressure fell by some 2 mm., corresponding to a formation of about 6 mm. of water vapour, according to the equation

$$2H_2 + O_2 = 2H_2O.$$
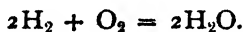
At the end of this period the water was introduced through the side arm, and the light was simultaneously shut off. After standing for 5 minutes the reaction vessel was removed, and the resulting solution of chlorine and hydrogen chloride tested for the presence of hydrogen peroxide with a solution of titanic acid. A clear positive result was obtained while control experiments using chlorine water and hydrogen chloride mixtures alone gave absolutely no effect. Comparison of the yellow colour obtained against that given by a standard solution of hydrogen peroxide indicated, however, that only a relatively small quantity of hydrogen peroxide was present, corresponding to a pressure of ·02 mm. in the original reaction vessel. The smallness of this quantity compared with the total water formation of 6 mm., suggests that the hydrogen peroxide was destroyed by the light almost as fast as it was formed, so that a photostationary state involving only a small concentration resulted. This point was confirmed by the following experiment :

(*b*) Approximately equal currents of hydrogen, chlorine and oxygen from cylinders, after bubbling through water and subsequent drying by calcium chloride and phosphorus pentoxide, were mixed, and rapidly streamed through a water jacketed glass tube, which was subjected to the light of two mercury vapour lamps. The outgoing gases containing hydrogen chloride, water, and hydrogen peroxide, were passed through 50 c.c. of water in a wash bottle which was kept screened from the light. The apparatus was made of glass throughout. After the gases had been streaming for about half an hour, the chlorine was shut off, and the dissolved chlorine displaced from the water in the wash bottle by a stream of hydrogen and oxygen. The solution was then tested with titanic acid, and gave a strong positive reaction for hydrogen peroxide. In a second experiment, in which the gases were passed for two hours, the hydrogen peroxide collected, after

[9] Klinkhardt and Frankenburger, *Z. physikal. Chem.*, **B 8**, 138, 1930.

diluting to five times the volume, was estimated colorimetrically with titanic acid against a standard solution. The amount collected was in this way found to be 0·0026 gms., a quantity equivalent to about 1·5 c.c. of $N/10$ H_2O_2 solution.

Control experiments using a similar gas stream without the light, and also a stream of hydrogen and oxygen only with the light on, indicated no trace of hydrogen peroxide. It is therefore clear that hydrogen peroxide in considerable quantities can be isolated when hydrogen, chlorine and oxygen are illuminated with visible and long wave ultra-violet light, provided precautions are taken to remove the products as rapidly as possible from the decomposing action of the light.

Conclusions.

These facts taken in conjunction with those cited above, make it probable that the action of oxygen in inhibiting the hydrogen chlorine reaction, lies in its reaction with the hydrogen atoms, according to the scheme

$$H + H_2 + O_2 = H_2O + OH$$
$$OH + OH + X = H_2O_2 + X'.$$
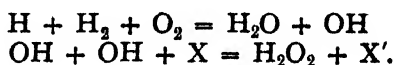
By this process both water and hydrogen peroxide are formed. It follows further that the OH radicle cannot participate in the hydrogen chlorine chain as postulated by Coehn and Jung[10] and therefore rules out the possibility of accounting for the catalytic action of water on such a basis. The author has pleasure in expressing his indebtedness to Dr. J. G. A. Griffiths for assistance with some of the experimental work recorded above.

Summary.

Reasons are given for supposing that the inhibiting action of oxygen in the photochemical reaction between hydrogen and chlorine is due solely to reaction of the oxygen molecules with the hydrogen atoms of the chains, with the formation of free hydroxyl radicles. On the basis of the recent work of Haber and others on the mechanism of the homogeneous reaction between hydrogen and oxygen, these hydroxyl radicles should combine at room temperature to give hydrogen peroxide. In confirmation of the above hypothesis, the production of hydrogen peroxide in appreciable quantities when mixtures of hydrogen, chlorine and oxygen, at atmospheric pressure are irradiated in glass apparatus by a mercury lamp has been demonstrated.

[10] Coehn and Jung, *Ber.*, **56B**, 696, 1923.

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THE PHOTOCHEMISTRY OF MIXTURES OF CHLORINE, OXYGEN, AND CARBON MONOXIDE.

By PROFESSOR G. K. ROLLEFSON (*Berkeley, Cal.*).

A little over a year ago Lenher and Rollefson[1] published a mechanism for the photochemical formation of phosgene. In this mechanism it was found necessary to introduce a molecule, $COCl$, as an intermediate compound which could react with chlorine to form phosgene or with oxygen to form carbon dioxide. The latter reaction was used to account for the inhibiting action of oxygen on the phosgene formation. This same intermediate compound, $COCl$, had been used by Bodenstein, Lenher and Wagner[2] in an earlier paper but in a somewhat different manner in that they considered that an equilibrium existed represented by the equation

$$COCl \rightleftarrows CO + Cl.$$

In their mechanism the phosgene was formed by triple collisions between chlorine atoms, carbon monoxide molecules, and chlorine molecules and the inhibiting effect of oxygen was attributed to a reaction with $COCl$ which caused a decrease in the concentration of chlorine atoms in the system. Lenher and Rollefson objected to the equilibrium shown above on the grounds that the $COCl$ molecule should react with chlorine as well as oxygen and therefore the equilibrium could not be maintained. Schumacher[3] has defended the views of Bodenstein, Lenher and Wagner, saying that the rate of formation of $COCl$ by triple collisions is reasonably fast at ordinary pressures and the heat of formation of $COCl$ is so low that the decomposition must proceed at a rapid rate. This is not a sufficient argument for the equilibrium as it is also necessary to show that all other reactions involving $COCl$ are slow relative to the formation and decomposition. That this is unlikely we can see by considering the reaction between chlorine and this intermediate. The rate of formation of $COCl$ will depend upon the number of triple collisions involving a CO molecule and a chlorine atom; according to the usual methods of calculation employed in kinetic theory this will be of the order of one one-thousandth of the total number of collisions a chlorine atom suffers. Now the newly formed $COCl$ molecule, in an equimolar mixture of CO and Cl_2, makes about half its collisions with chlorine molecules; therefore if one in five hundred such collisions is effective in causing reaction to form phosgene the rate of such a reaction would be equal to the rate of formation of $COCl$, thus making it impossible for $COCl$ to be at its equilibrium concentration. This also answers Schumacher's contention that the two methods of forming phosgene, namely,

$$CO + Cl_2 + Cl = COCl_2 + Cl$$

and

$$COCl + Cl_2 = COCl_2 + Cl$$
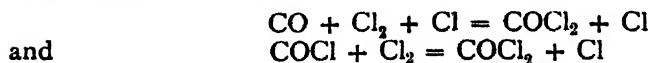
[1] Lenher and Rollefson, *J. Am. Chem. Soc.*, **52**, 500, 1930.
[2] Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **B3**, 459, 1929.
[3] Schumacher, *J. Am. Chem. Soc.*, **52**, 3132, 1930.

are kinetically identical since that is true only if COCl is in equilibrium with carbon monoxide and chlorine atoms. The other points which have been discussed in previous papers will not be touched on here as the principal object of this paper is to outline an experimental test of the mechanism of Lenher and Rollefson and give some preliminary results which have been obtained.

The mechanism with which we shall deal consists of the following reactions

$$Cl_2 + h\nu = Cl + Cl^*. \qquad . \qquad . \qquad . \qquad (1)$$
$$Cl + CO + Cl_2 = COCl + Cl_2 \qquad . \qquad . \qquad (2)$$
$$COCl + Cl_2 = COCl_2 + Cl \qquad . \qquad . \qquad (3)$$
$$COCl + Cl = CO + Cl_2 \qquad . \qquad . \qquad . \qquad (4)$$
$$COCl + O_2 = CO_2 + ClO \qquad . \qquad . \qquad . \qquad (5)$$
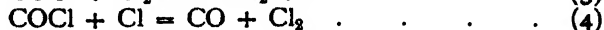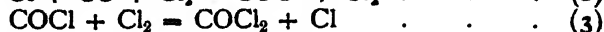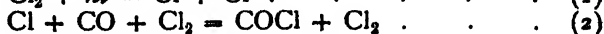
The steps following (5) in the CO_2 formation are omitted as they are not definitely established and are not essential to the present discussion. An inspection of these equations shows that the formation of carbon dioxide proceeds by the same mechanism as that of phosgene up to the stage [4] where we have COCl and therefore the relative amounts of the two products will depend upon the manner in which the COCl molecules divide between the two paths. The kind of results which we should obtain in a case like this may be predicted by a comparison with the most simple case of the type which we can find, namely, the quenching of fluorescence by the addition of gases. In that case we may represent the processes involved by the equations

$$A^* = A + h\nu$$
$$A^* + M = A + M$$
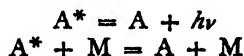
That is, we have the activated molecules, A^*, returning to the normal state with the emission of light or being deactivated by collision with some molecule M. The relative amounts of the two processes in this case are well known from the results in the literature. In the present case we do not have any fluorescence but we may speak of the COCl molecule as having a certain life period with respect to its reaction with chlorine. Now if we take a definite pressure of chlorine and vary the pressure of the oxygen the fraction of the total number of COCl molecules formed that react with chlorine will decrease as the oxygen pressure increases much as the intensity of fluorescence is decreased by the addition of a foreign gas. Experimentally this can be studied by determining the relative amounts of CO_2 and $COCl_2$ formed as the ratio of the oxygen and chlorine pressures is varied. It is experiments of this type that are being carried out and are yielding results as predicted.

The experimental technique involved is extremely simple, consisting of illuminating mixtures of chlorine, oxygen and carbon monoxide and determining the amounts of the two products from the pressure change at room temperature and also after freezing out condensible gases with liquid air. In order to show how this is done, consider the two reactions

$$2CO + O_2 = CO_2$$
$$CO + Cl_2 = COCl_2$$
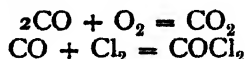
Let Δp_1 be the pressure change due to CO_2 formation and Δp_2 be that due to $COCl_2$ formation. The total pressure change is $\Delta p = \Delta p_1 + \Delta p_2$. One

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[4] It is quite possible that oxygen molecules may supplement the action of the chlorine molecules in reaction (2), but the experimental data available at the present time are not capable of deciding this point.

other equation involving Δp_1 and Δp_2 will suffice for the determination of these two quantities. To obtain this consider the changes in the sum of the CO and O_2 pressures which we shall represent by $\Delta(CO + O_2)$.

$$\Delta(CO + O_2) = 3\Delta p_1 + \Delta p_2.$$

Combining this with our previous equation

$$\Delta p_1 = \tfrac{1}{2}[\Delta(CO + O_2) - \Delta p]$$
$$\Delta p_2 = \Delta p - \Delta p_1.$$

Since CO_2, Cl_2 and $COCl_2$ all have very low vapour pressures at liquid air temperatures the pressure measured when the reaction vessel is immersed in liquid air is that of the CO and O_2. The value of $\Delta(CO + O_2)$ may be obtained by immersing the reaction vessel in liquid air before and after a period of illumination, reading the change in pressure, and calculating the value of $\Delta(CO + O_2)$ at room temperature by means of an experimentally determined factor. This factor varies slightly with the temperature of the liquid air but was usually about 3·2. Table I. gives the results obtained for mixtures illuminated at 19° C. The chlorine pressure was 35 cm. of sulfuric acid or slightly less than 5 cm. of mercury.

TABLE I.

$\dfrac{O_2}{Cl_2}$	$\dfrac{\Delta O_2}{\Delta O_2 + \Delta Cl_2}$	$\dfrac{\Delta Cl_2}{\Delta O_2 + \Delta Cl_2}$
1·17	0·955	0·045
1·10	·90	·10
1·06	·88	·12
·96	·88	·12
·87	·86	·14
·81	·80	·20
·77	·80	·20
·54	·74	·26
·49	·76	·24
·45	·70	·30
·26	·60	·40
·21	·55	·45
·18	·52	·48
·15	·48	·52

Although there are some fluctuations it is apparent that the results are in accord with the discussion given above. A more complete account of the experiments will be published as soon as the work has been carried out over a wider range of conditions.

Summary.

An experimental test of the mechanism for the photochemical formation of phosgene proposed by Lenher and Rollefson has been described and some preliminary results presented which are in favour of that mechanism. Reasons have been given for considering that the molecule COCl involved in the mechanism cannot be in equilibrium with carbon monoxide and chlorine atoms.

GENERAL DISCUSSION.

Professor M. Bodenstein (*Berlin*) said : I do not at all agree with the contents of Professor Rollefson's paper; for the following reasons :—

(1) We have never assumed that if oxygen is present the equilibrium $COCl \rightleftharpoons CO + Cl$ should be established. That is true if there is no oxygen.

(2) The mechanism suggested by the author seems to me to be an example of the kind of thing I have mentioned in my introductory paper. This mechanism claims to give an explanation only for a limited number of observed facts—although even this claim is not correct, because the assumption, that it is exclusively the chlorine molecules which are able to stabilise the quasi-molecules of COCl, is by no means supported by any known analogies—as has already been shown by Schumacher in the paper mentioned by Rollefson. By using a series of intermediate reactions differing from those of this author we have been able to calculate quantitatively all the velocity constants of these reactions, in close agreement with all the many various facts observed with this curious reaction. A paper dealing with this calculation will shortly be published.

THE MECHANISM OF THE PHOTO-OXIDATION OF GASEOUS ALKYL HALIDES.

By John Reginald Bates and Robert Spence.

Increased knowledge of the significance of absorption spectra, in regard to the primary process following light absorption, has proved to be of great aid in determining the mechanism of photochemical reactions. According to the theory of Franck,[1] continuous absorption indicates a dissociation as the primary process. Among the molecules showing this type of spectrum may be cited the hydrogen and alkyl halides.[2] The former yields hydrogen and halide atoms while the latter may be shown, not only from analogy, but also from energetic and structural considerations to give an alkyl group and a halide atom. Consequently, elucidation of the kinetics of their photochemical decomposition and oxidation should at once demonstrate the validity of the Franck theory, and furnish a great deal of valuable information regarding the oxidation of free alkyl groups. Methyl iodide was chosen for investigation because of the convenience of its absorption spectrum, and more particularly because of the added simplification brought about by the low vapour pressure of iodine, which could be progressively removed from the reaction zone.

Photo-chemical Decomposition of Methyl Iodide.

Methyl iodide, when exposed to the light of a mercury arc, reacts, as determined by total pressure decrease, iodine and non-condensable gas formed, at an extremely slow rate. A Budde effect, similar to that occurring in chlorine, was observed.

Photo-oxidation of Methyl Iodide at 0° C.

Upon the addition of oxygen to methyl iodide, the rate of pressure decrease became over a hundred fold greater and permitted of kinetic

[1] Franck, *Trans. Farad. Soc.,* 21, 536, 1925.
[2] Herzberg and Scheibe, *ibid.,* 25, 716, 1928; *Z. physik. Chem.* (B) 7, 390, 1930; Mills and Iredale, *Nature,* p. 604, October, 1930.

measurements. Excepting the window, all of the reaction vessel was immersed in a mixture of ice and water, allowing the iodine, etc., to condense on the walls away from the window. Measurement of pressure change and titration of iodine liberated after given periods, established the relation between mm. of methyl iodide used and mm. of total pressure decrease accompanying the reaction. Almost exact correspondence was observed for the initial thirty mm. of reaction, to which all the subsequent kinetic measurements were confined.

The products of oxidation were paraformaldehyde, methylal, water and iodine which were shown by analysis to be present in the proportions required by the following equation :

$$4CH_3I + 2O_2 \rightarrow (CH_3O)_2CH_2 + (CH_2O)n + H_2O + 2 I_2.$$
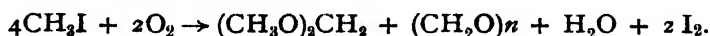
Kinetics.—By interposing screens which cut down the light intensity by known fractions, the rate of reaction at different light intensities was measured and found to be directly proportional to the light intensity. The influence of varying methyl iodide concentrations is shown in Table I. and obeys the following exponential expression :

$$\frac{dx}{dt} \sim I_{abs.} = I_0(1 - e^{-0.047[CH_3I]}).$$

At constant methyl iodide concentration, the rate increases very rapidly with oxygen from zero initial concentration, finally reaching a maximum value, after which it is independent of oxygen (Table II.).

TABLE I.—Dependence of Rate on Methyl Iodide Concentration.

CH₃I mm.	O₂ mm.	dx/dt.	K.	CH₃I mm..	O₂ mm.	dx/dt	K.
9·9	100·7	1·88	5·68	70·1	101·0	4·13	4·81
19·8	102·7	2·15	3·98	79·2	101·6	4·20	4·82
29·1	100·2	2·95	4·44	89·6	100·4	4·25	4·83
59·7	100·2	3·70	4·42	99·5	107·4	4·03	4·53

TABLE II.—Dependence of Rate on Oxygen Concentration.

CH₃I mm.	O₂ mm.	dx/dt.	K.	CH₃I mm.	O₂ mm.	dx/dt.	K.
15·0	10·1	1·25	5·46	15·2	101·2	2·14	4·73
15·6	11·2	1·20	4·85	15·1	245·9	2·24	4·62
15·5	50·7	1·51	3·63	15·7	388·1	2·30	4·56
40·1	10·4	1·60	4·11	38·8	98·7	3·42	4·58
40·0	19·6	2·65	5·07	40·7	100·2	3·54	4·68
41·8	31·3	2·80	4·53	40·0	204·9	4·00	4·99
39·2	39·3	3·27	5·05	39·4	299·3	4·18	5·02
40·1	39·4	3·10	4·79	40·8	446·8	4·05	4·89
39·5	41·3	3·27	4·99	39·3	614·2	4·00	4·80
61·6	5·3	1·29	4·53	60·6	102·5	3·98	4·73
61·6	21·0	3·33	5·59	60·5	103·0	3·92	4·66
60·5	50·3	3·89	5·14	59·7	409·1	4·26	4·67

These results are expressed in the following equation :

$$\frac{dx}{dt} = K\frac{(1 - e^{-0.047\,CH_3I})[O_2]}{12.3 + [O_2]}.$$

and the values of K are given in the last column of Tables I. and II.

An approximate quantum yield, obtained by an actinometric method using chloracetic acid, which is known to have a quantum yield[3] of one at about 2500 Å., gave a value of 2.2 molecules per $h\nu$. A more detailed account of the above results will appear in a forthcoming issue of the *Journal of the American Chemical Society*.

Temperature Coefficent of the Reaction.—The close correspondence between P and mm. of methyl iodide reacting at $0°$ C., is purely fortuitous and when the reaction was carried out at other temperatures, the ratio between ΔP and mm. CH_3I reacting, changed. Therefore, the rate was measured by the total amount of iodine liberated in a given time. These values at different temperatures, corrected to standard light intensity I_0 are given in Table III.

TABLE III.—RATE OF REACTION OF 60 MM. CH_3I AND 30 MM. O_2 ILLUMINATED FOR 40 MINS. AT DIFFERENT TEMPERATURES.

$T°C.$	Gm. Mol. $I_2 \times 10^8$.				Average.	CH_3I mm.	I_0/I.	dx/dt.
− 10	15.8	16.8	16.2	15.4	16.05	11.9	1.23	3.51
0	14.9	14.2	14.7	14.0	14.45	10.25	1.23	3.15
10	10.8	12.5	11.9	10.7	11.50	8.16	1.23	2.51
20	10.9	10.9	9.3	8.4	9.90	7.02	1.23	2.16

Theoretical.

Decomposition of Methyl Iodide.—From the nature of the absorption spectrum, we may assume the primary process to be

$$CH_3I + h\nu \rightarrow CH_2 + I' \qquad (a)$$
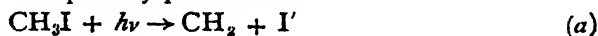
and

$$-\frac{d[CH_3I]}{dt} = I_0(1 - e^{-\alpha[CH_3I]})$$

will represent the rate of this reaction where I_0 is the light intensity, and α is the product of the absorption coefficient and the thickness of the gas traversed by the light. Strictly speaking, the α's and I's should be taken for every wave-length, but the equation will hold very closely for the whole band.

In the absence of oxygen, the following three body or wall reactions may take place :

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M' \qquad (b)$$
$$CH_3 + I + M \rightarrow CH_3I + M' \qquad (c)$$
$$I + I + M \rightarrow I_2 + M' \qquad (d)$$
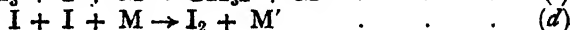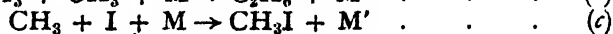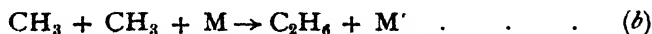
accompanied by a series of bimolecular reactions :

$$CH_3 + I_2 \rightarrow CH_3I + I \qquad (e)$$
$$CH_3 + I \rightarrow CH_2 + HI \qquad (f)[4]$$
$$CH_3 + CH_3I \rightarrow C_2H_6 + I \qquad (g)$$
$$CH_3 + CH_3 \rightarrow CH_4 + CH_2 \qquad (h)$$

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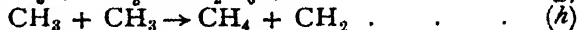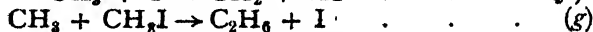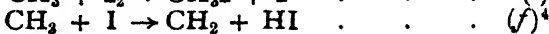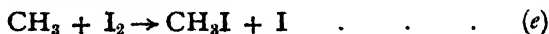
[3] Rudberg, *Z. Physik*, **24**, 247, 1924.
[4] The second hydrogen atom stripped from a carbon atom has a heat of linkage of only 30 cal. Mecke, *Z. Elektrochem.*, **36**, 595, 1930.

On the other hand, the reactions

$$I + CH_3I—CH_3 + I_2(- 33 \text{ Cal.})$$
$$I + CH_3I—CH_2I + HI(- 41 \text{ Cal.})$$
$$I + CH_3I—CH_2I_2 + H(- 42 \text{ Cal.})$$
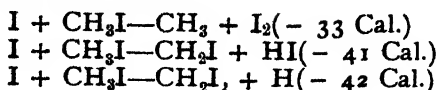
are thermally impossible if we accept the value $C - H = 110$ Cal.; $H - I = 69$ Cal.; $I - I = 35$ Cal.; and $C - I = 68$ Cal., for the heats of linkage.[4]

The very slow rate of formation of permanent gas and free iodine indicates that (*b*) and (*g*) must be of relatively infrequent occurrence. Under these circumstances, the majority of the methyl groups must reform methyl iodide by (*e*) and the wall reaction (*c*), while the remainder will form ethane according to (*b*) and (*g*), with (*f*) and (*h*) occurring very seldom, owing to the low concentrations of CH_3 and I. At first sight, reaction (*b*) might be expected to occur at least as frequently as (*d*), but when the wall is covered with iodine, the probability of (*c*) and (*e*) occurring will be enormously increased at the expense of (*b*). It is interesing to note that reaction (*g*) cannot be a very probable one in spite of its exothermicity, and this, if we may regard methyl as a pseudo halogen, provides another example of an elementary process which does not go on every collision. Recently, several similar cases have been cited in the literature [5] and Polany's conclusion that the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$
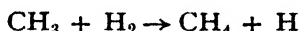
occurs only once in every 10^6 collisions at $0°$ C. and requires an activation energy of 8 Cal. has been confirmed by our observation that addition of hydrogen to methyl iodide did not materially affect the reaction.

Oxidation of Methyl Iodide.—Besides those reactions possible in methyl iodide alone, when oxygen is present, methyl groups may be removed by reacting with oxygen, and since the oxidation reaction occurs over a hundred times faster than the decomposition, we may neglect (*b*), (*f*), (*g*) and (*h*) from our kinetic considerations. In these circumstances, the following reactions can occur :—

$$CH_3 + h\nu \rightarrow CH_3 + I' \quad . \quad . \quad . \quad . \quad (1)$$
$$CH_3 + I_2 \rightarrow CH_3I + I \quad . \quad . \quad . \quad . \quad (2)$$
$$CH_3 + I + M \rightarrow CH_3I + M' \quad . \quad . \quad . \quad . \quad (3)$$
$$I + M(I) \rightarrow I_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$
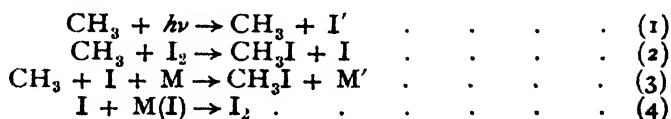
Reaction (4) is obtained from (*d*) since iodine atoms are cleaned up on the walls,[6] and methyl groups are oxidised by

$$CH_3 + O_2 \rightarrow CH_2O + OH \quad . \quad . \quad . \quad (5)$$
$$OH + CH_3I \rightarrow CH_3OH + I \quad . \quad . \quad . \quad (6)$$
$$2CH_3OH + CH_2O \rightarrow CH_2(OCH_3)_2 + H_2O \quad . \quad . \quad (7)$$
$$nCH_2O \rightarrow (CH_2O)n \quad . \quad . \quad . \quad (8)$$
$$nCH_2O + h\nu \rightarrow (CH_2O)n \quad . \quad . \quad . \quad (9)$$
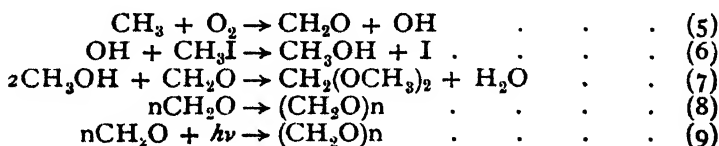
Reactions (7) and (8) are possible, because the authors have shown that methyl alcohol and formaldehyde condense together very rapidly in the dark at $0°$ C., while formaldehyde polymerises slowly in the dark and more rapidly in ultra-violet light at $0°$ C.

[5] Kistiakowsky, *J. Am. Chem. Soc.*, **52**, 1868, 1930; von Wartenburg and Taylor, *Nachr. Gött. Akad.*, 119, 1930 ; Franck and Rabinowitsch, *Z. Elektrochem.*, 36, 794, 1930 ; Hartel and Polanyi, *Z. physik. Chem.*, B 11, 97, 1930.
[6] Bonhoeffer and Farkas, *Z. physik. Chem.*, 132, 235, 19:8.

This reaction series leads directly to the following kinetic equation

$$- \frac{d[CH_3I]}{dt} = \frac{2 \cdot k_1 I_0 (1 - e^{-\alpha[CH_3I]}) [O_2]}{\frac{k_2}{k_5}[I_2] + [O_2]},$$

which becomes identical with the experimentally determined equation when we insert the vapour pressure of iodine at 0° C. (0·03 mm.) and put k_2/k_5 equal to 410.

The possibility of an alternative mechanism involving the formation of a peroxide was considered, since this type of compound has frequently been detected among the products of the slow oxidation of hydrocarbons.[7] The formation of a peroxide would necessitate the intervention of a third body thus :—

$$P + CH_3 + O_2 \rightarrow CH_3O_2 + P' \qquad . \qquad . \qquad . \quad (5')$$
$$CH_3I + CH_3O_2 \rightarrow CH_2O + CH_3OH + I \quad . \qquad . \quad (6')$$
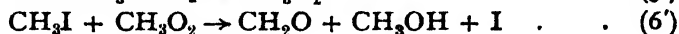
Such a mechanism leads to the equation

$$- \frac{d[CH_3I]}{dt} = \frac{2 \cdot k_1 I_0 (1 - e^{-\alpha[CH_3I]}) [O_2]}{\frac{k_2'[I_2]}{k_5'[P]} + [O_2]},$$

where $[P]$ is the total pressure. According to this, increase in total pressure at low oxygen concentration should increase the rate. Comparing the relative rates predicted by the two mechanisms for methyl iodide (50 mm.) and oxygen (10 mm.) with methyl iodide (50 mm.), oxygen (10 mm.) and nitrogen (40 mm.), we should expect the rates to be in the ratio of 1 : 2·35 (assuming that nitrogen would be effective in the three body process of peroxide formation). The experimental ratio is 1 : 0·9 thus favouring the " hydroxyl " mechanism.

The value of k_2/k_5 is of great interest, since it indicates that reaction (5), between methyl group and oxygen, though strongly exothermic, goes at a rate of about 1/410 at 0° of that of reaction (2) between methyl group and iodine. To determine the relative probability of these processes in terms of the ratio of effective collisions to the total number, we must make use of the expression :—

$$\frac{k_2}{k_5} = \frac{\nu_2 a_2}{\nu_5 a_5} e^{\frac{Q_5 - Q_2}{RT}},$$

where ν_2 and ν_5 are the number of collisions per second of methyl with iodine and with oxygen respectively, a_2 and a_5 are constants involving a steric factor which we assume to be approximately equal for iodine and oxygen. The ratio ν_2/ν_5 obtained from the gas kinetic equations, assuming methyl to have the same gas kinetic diameter as methane, is equal to 1/0·9, i.e.,

$$e^{\frac{Q_5 - Q_2}{RT}} = 0·9 \, k_2/k_5 = 369.$$

Hence, $Q_5 - Q_2 = 3210$ Cal., i.e., the heat of activation of $CH_3 + O_2$ cannot be less than 3000 Cals. although the reaction is 80 Cal. exothermic. This value will change by the average increase in kinetic energy with

[7] Callendar, *Engineering*, **123**, 147, 182, 210, 1927 ; Brunner and Rideal, *J. Chem. Soc.*, 1162, 1928 ; Bone and Hill, *Proc. Roy. Soc.*, A **129**, 434, 1930 ; Fort and Hinshelwood, *ibid.*, A **129**, 284, 1930.

temperature, which is equal to $3RT = 60$ Cal. per $10°$ C. for a bimolecular process.   Using the equation,

$$\log P_{atm.} = -\frac{3512 \cdot 3}{T} - 2 \cdot 013 \log T + 13 \cdot 374,$$

given by Giauque [8] for the vapour pressure of iodine at a given temperature, we can calculate the quantity $A = k_1 I_0 (1 - e^{-\alpha[CH_3I]})$ from the rate at different temperatures, given in Table III., and from the expression :—

$$A = \frac{dx}{dt} \frac{\frac{k_2}{k_3}[I_2] + [O_2]}{[O_2]}.$$

TABLE IV.—CONSTANCY OF A AT DIFFERENT TEMPERATURES ASSUMING $Q_5 - Q_2$.

$T°$ C.	$Q_5 - Q_2$.	k_2/k_3.	A.
− 10	3270	582	4·25
0	3210	410	4·44
10	3150	300	4·59
20	3090	230	5·52

If, instead of calculating A, we assume $k_1 I_0$ to be constant and equal to its maximum value of 4·72, we obtain the following results :—

TABLE V.—VALUES OF $Q_5 - Q_2$ ASSUMING A TO BE CONSTANT.

$T°$ C.	$Q_5 - Q_2$	k_2/k_3.	A.
− 10	3390	728	4·43
0	3205	406	4·43
10	3105	277	4·43
20	2876	155	4·43

The values for − 10°, 0°, and 10° C. are in excellent agreement, but those at 20° appear to be abnormal, possibly owing to an unobserved increase in light intensity during some of the experiments at this temperature.

We can, therefore, now write our kinetic formula, in a form which takes account of light intensity, size of vessel, concentration of reactants and temperature :—

$$-\frac{d[CH_3I]}{dt} = \frac{2 I_0 (1 - e^{-\cdot 0036\, d[CH_3I]})\,[O_2]}{e^{\frac{3210}{RT}}[I_2] + [O_2]},$$

where d is the length of the reaction vessel in cms. and concentrations are measured in mm. Hg.   The general significance of this result for gaseous oxidations in general should not be overlooked, for there is a close relationship between the above formula and the empiric one discovered by Spence and Kistiakowsky [9] for the oxidation of acetylene, and a still closer similarity to the equation proposed by Bodenstein [10] for the thermal oxidation of acetaldehyde,

$$-\frac{d[CH_3CHO]}{dt} = k_1 \frac{[CH_3CHO] k_4 [CH_3CHO]}{k_5[O_2] + k_6}.$$

[8] Giauque, *J. Amer. Chem. Soc.*, **53**, 507, 1931.
[9] Spence and Kistiakowsky, *J. Amer. Chem. Soc.*, **52**, 4837, 1930.
[10] Bodenstein, *Sitz. preuss. Akad. Wiss.* (in the press).

Considerable support for the "hydroxyl" theory already exists, for Bonhoeffer and Haber [11] have demonstrated the presence of free hydroxyl in flames, while Lavin and Jackson [12] have shown that hydroxyl groups can bring about the oxidation of carbon monoxide at room temperature. Ethyl iodide has an approximately similar rate of photochemical oxidation to methyl iodide but gives acetaldehyde, polymerised acetaldehyde, iodine and ethyl alcohol as products. Ethyl alcohol was identified by applying the iodoform test to the fraction of the liquid product boiling between 70°-80° C. Iodoform separated upon warming, whereas acetal (B.P. 104° C.) requires previous acidification of the solution. Another portion of the liquid product gave ethyl acetate when heated with glacial acetic acid and sulphuric acid.

One of the authors (R. S.) wishes to express his thanks to the Commonwealth Fund for a Fellowship.

Summary.

A kinetic study of the photochemical oxidation of methyl iodide has shown that the effect of changing light intensity, concentration of reactants and temperature can be adequately explained by a kinetic formula deduced from the proposed mechanism. The quantum yield and the products of the reaction are also in accord with the theory.

[11] Bonhoeffer and Haber, *Z. physik. Chem.*, **137**, 263, 1928.
[12] Lavin and Jackson, *J. Amer. Chem. Soc*, **53**, 383, 1931.

Princeton, New Jersey.

A COMPARISON OF THE EFFICIENCY OF PHOTO-CHEMICAL REACTIONS AND SIMILAR REACTIONS PRODUCED BY GASEOUS IONS.

BY G. R. GEDYE, *Laboratory of Physical Chemistry, Cambridge.*

The amount of energy liberated in the recombination of gaseous ions is in general larger than the quanta corresponding to the wavelengths normally employed in photochemical reactions, and thus results in a higher degree of activation of the molecule. Recent work by Lind [1] and his co-workers has shown, however, that in several chain reactions the yield per quantum is nearly equal to the yield per ion-pair over a wide range of experimental conditions. This shows that after differently initiated primary processes, similar chains are propagated. There is also available a certain amount of data which enables comparison to be made in the case of reactions not associated with a chain mechanism, and in this paper three reactions of this class are discussed.

1. The Decomposition of Ammonia.—Wourtzel,[2] who examined this reaction under the action of α-particles calculated the number of molecules decomposed per ion-pair, commonly denoted by M/N, over a considerable

[1] Alyea and Lind, *J.A.C.S.*, **52**, 1853, 1930.
[2] Wourtzel, *Le Radium*, **11**, 289, 332, 1919.

range of temperatures.   A correction should be applied to his figures to allow for the deposition of the radioactive deposits on the walls of the reaction vessel during the experiment,[24] and the corrected values are given in Table I.

TABLE I.			TABLE II.	

Temperature.	M/N.		Temperature.	Quantum Efficiency. γ
18° C.	1·24		20° C.	0·4
108° C.	2·45		100° C.	0·7
220° C.	3·6		200° C.	0·9
315° C.	4·0		300° C.	1·4
			400° C.	2·5
			500° C.	3·3

A similar effect (Table II.) was observed by Kuhn[3] in the photochemical reaction.

It is to be noted that the quantum efficiency over the range investigated by both methods is rather less than half the ion-pair efficiency.

The results of Wourtzel were confirmed by Gedye and Allibone[4] using high velocity electrons.   They calculated that $M/N = 1\cdot2$ at ordinary temperatures.   At low pressures a considerable fraction of the ammonia was converted into hydrazine, an observation paralled by that of Bredig, Koenig and Wagner,[5] with the silent discharge.   There is also strong evidence to support the view that ammonia first dissociates into NH and H_2 or 2H, and that hydrazine is formed by union of NH and NH_3.   In the first place Kneser[6] photographed the spectrum of ammonia, streamed through the glow discharge at low pressures.   Near the entry of the gas the most prominent bands were the Schuster bands at 5635 and 5670 Å., and an ultra-violet band at 3360 Å.   In the central portion of the tube the former disappeared, leaving only the ultra-violet band, while at the end this also disappeared, only the spectrum of nitrogen and hydrogen being observed. This band at 3360 has been observed by a number of authors.[7]   Hulthèn and Nakamura[8] analysed the spectrum and showed it was probably due to NH, and their conclusion was supported by Gaviola and Wood,[9] who obtained it by mercury sensitisation.   Secondly Lavin and Bates[10] showed that when ammonia was streamed through a discharge tube an active gas was obtained, differing in its properties from active nitrogen and hydrogen. It reduced certain metallic oxides and reacted with solid ammonia at the temperature of liquid air, with chemi-luminescence.   Evidence was also obtained for formation of atomic hydrogen.

It may therefore be concluded that NH is formed in the decomposition of ammonia, and then enters into reaction with ammonia to form hydrazine. The reaction

$$NH + NH_3 = N_2H_4$$
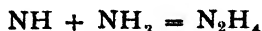
is almost certainly highly exothermic and could not take place unless a third body were present to remove the energy of reaction.   Thus it

[3] Kuhn, *C.R.*, **178**, 708, 1924.
[4] Gedye and Allibone, *P.R.S.*, A **130**, 346, 1931.
[5] Bredig, Koenig and Wagner, *Z. physik. Chem.*, A **139**, 211, 1928 ; A **144**, 213, 1929
[6] Kneser, *Ann. Physik*, **79**, 585, 1926.
[7] Lewis, *Astrophys. J.*, **40**, 154, 1914 ; Fowler and Gregory, *Phil. Trans.*, **218**, 315, 1919; Barratt, *P.R.S.*, **98**, 40, 1920.
[8] *Nature*, **119**, 235, 1927.   [9] *Phil. Mag.* (VII.), **6**, 1191, 1928.
[10] *Nature*, **125**, 709, 1930 ; *Proc. Nat. Acad. Sci.*, **16**, 804, 1930.

should proceed largely on the surface of the vessel, or on dust particles. This would explain the long life of the gas observed by Lavin and Bates, and the reaction with solid ammonia.   It also provides a possible explanation of the fact that hydrazine is formed preferentially at low pressures, if there is a concurrent gas reaction   .

$$NH + NH_3 = N_2 + 2H_2$$
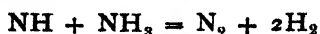
in which only a small proportion of the collisions are effective.

The similar effect of temperature in the two cases strongly suggests that the mechanism in the two cases is similar.   Dickenson and Mitchell [10a] who investigated the mercury sensitised decomposition of ammonia, observed an ultra-violet band with a maximum at 3370 Å.   Thus there is direct evidence for the formation of NH in the photosensitised decomposition.   Kassel and Noyes [11] using radiation of wavelength 1600-1900 Å. found a quantum efficiency of 0·7, a value somewhat higher than that of Kuhn.   Thus the quantum efficiency appears to increase with decreasing wavelength, that is, with increasing energy of activation.

The recombination of the NH_2^+ ion and an electron liberates 11·1 electron-volts which corresponds to a wavelength of 1110 Å.   Thus, the still higher efficiency in the ionic reaction may be, at all events partly, accounted for by the higher degree of activation of the molecule.   Further it is possible that two molecules, a positive and a negative ammonia ion, may be concerned in the primary process, whereas the work of Bonhoeffer and Farkas [12] on the predissociation spectrum of ammonia proves that only one molecule is concerned in the primary process in the photochemical reaction.   The primary reaction

$$NH_3 = NH + H_2$$

in the photochemical reaction is quite plausible on thermochemical grounds. The heat of formation of NH from N and H has been calculated by Villars [13] to be about 4·7 electron-volts.   Taking 9·0 and 4·3 electron-volts as the heats of formation of N_2 and H_2 respectively we obtain for the reaction

$$NH_3 = NH + H_2$$

an absorbtion of approximately 2·5 electron volts.   Predissociation begins at 2200 Å, which corresponds to a quantum of 5·6 electron-volts.

H. S. Taylor [14] has suggested the alternative primary mechanism

$$NH_3 = NH_2 + H$$

for the photochemical reaction, and has investigated the reaction in the presence of ethylene which is known to be polymerised in the presence of atomic hydrogen.   It is to be noted, however, that in the mercury sensitised reaction between ethylene and hydrogen the main products are saturated hydrocarbons, while in the case of sensitisation by ammonia the complex hydrocarbons formed are mainly unsaturated.

2. The Decomposition of Nitrous Oxide.—In the photochemical reaction, Macdonald [15] showed that reaction proceeded according to the equation

$$4N_2O = 2NO + O_2 + 3N_2$$

[10a] Proc. Nat. Acad. Sci, 12, 692, 1926.
[11] J. Amer. Chem. Soc., 49, 2495, 1927.
[12] Z. physik. Chem., 134, 337, 1928.   [13] J.A.C.S., 51, 2374, 1929.
[14] Taylor and Emeléus, J.A.C.S., 53, 562, 1931.
[15] J.C.S., 1, 1928.

with a quantum efficiency of 3·9. I have investigated the same reaction under the action of cathode rays, and have found the reaction follows the same course. The ion-pair efficiency has been calculated, as in the case of the ammonia decomposition, on the assumption that the total ionisation relative to air for α-particles and cathode rays is the same.

The results obtained are given in Table III.

TABLE III.

Initial Pressure cms. Hg.	Time, mins.	Current Microamps.	Yield Nitrogen c.c. N.T.P.	Mols. Decomp. per Electron.	Electron Volts per Mol.
73·0	10	0·345	0·205	5·70 × 10³	7·8
73·0	10	0·337	0·20	5·65 ,,	7·9
73·0	10	0·286	0·16	5·36 ,,	8·3
73·0	10	0·524	0·305	5·58 ,,	8·0
66·0	10	1·01	0·655	5·75 ,,	7·7
					Mean 7·9(4)

Taking Eisl's[16] value of 32·2 electron-volts per ion-pair in air, and the relative total ionisation in N_2O as 1·02 we obtain 31·6 electron-volts per ion-pair in nitrous oxide, giving an ion-pair efficiency of 4·0. The agreement with Macdonald's results is very satisfactory, and points strongly to a similar mechanism after the primary activation process in each case.

There is insufficient data available to decide on the probable mechanism of the reaction. An examination of the ultra-violet absorbtion spectrum of nitrous oxide in the region in which photochemical reaction occurs should give definite evidence on whether predissociation occurs. If, on the other hand, Lind's[17] suggestion is correct that in both cases a cluster is formed on an excited or ionised molecule, the excited molecule must possess a longer life, and further the rate of the photochemical reaction should fall off at low pressures at which deactivation is probable before clustering is complete. It is to be noted that the reaction

$$N_2O = NO + N - 4·5 \text{ electron-volts}$$
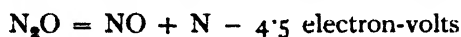
would be quite possible for a quantum corresponding to the wavelength used by Macdonald, viz. 1860-1990 Å. (1900 Å corresponds to a quantum of 6·5 electron-volts.)

III. The Formation and Decomposition of Ozone.—For the formation of ozone Warburg[18] found a quantum efficiency of 3 for a wavelength of 2070 Å, while Lind and Bardwell,[19] whose results are somewhat variable owing to the rapid reverse reaction, obtained values ranging from 1·5-2·6 per ion-pair. The agreement of the quantum and ion-pair efficiencies shows that a similar mechanism, after the primary activation process, is probable for the two cases. The reverse reaction is one in which the quantum and ion-pair efficiencies are very different. Marshall[20] and Busse and Daniells[21] showed that equilibrium under the action of cathode rays corresponds to about 0·1 per cent. formation of ozone. Taking 2 or 3 as the most probable value of the ion-pair efficiency in the formation of ozone, it appears that decomposition involves a chain of considerable length. In the photochemical decomposition, on the other hand, the quantum efficiency

[16] *Ann. Physik*, **3**, 227, 1929.
[18] *Sitz. Preuss. Akad.*, 644, 1913.
[20] *J.A.C.S.*, **50**, 3178, 1928.
[17] *J. physical Chem.*, **32**, 573, 1928.
[19] *J.A.C.S.*, **51**, 2751, 1929.
[21] *J.A.C.S.*, **50**, 3271, 1928.

approximates to two.[22]   It is important to note, however, that under certain conditions a chain may be initiated in the photochemical decomposition, since it was observed by Bonhoeffer,[23] that when reaction was sensitised by bromine as many as 30 molecules were decomposed per quantum. Thus this reaction provides an interesting case in which the high degree of activation occurring in ionisation results in the initiation of a chain, while in general photochemical activation does not.

I am much indebted to Professor E. K. Rideal for his advice and interest, and to Dr. T. E. Alliborne for his co-operation in the experimental work.

[22] Kistiakowsky, *Z. physik. Chem.*, **117**, 337, 1925.
[23] *Z. Physik*, **13**, 94, 1923.
[24] Mund, *J. physical Chem.*, **30**, 894 (footnote), 1926.

GENERAL DISCUSSION.

Dr. W. Frankenburger (*Ludwigshafen*) said : In connection with Mr. Gedye's remarks upon the decomposition of NH_3 into NH and H_2 brought about by irradiation and by bombardment with a-particles, I would remark briefly that, according to at present unpublished researches at Oppau, the *thermal* decomposition of NH_3 molecules which are adsorbed on the surface of a metallic catalyst such as tungsten takes place, at moderate temperatures ($\sim 90°-200°$ C.), in two ways.   On the more active spots (the number of which depend upon the nature and treatment of the metal as well as on temperature) the NH_3 molecules give up, in a single primary process, the whole of the hydrogen, and the nitrogen remains to all appearances combined with the metal as "surface nitride."   At the less active spots there is produced for each molecule of NH_3 one molecule of H_2 so that an imide-like metal compound remains behind.   The nitrogen will only be given up by the metal at considerately higher temperatures ($600°-800°$ C.).   A decomposition in the direction of the process $NH_3 \rightarrow NH_2 + H$ can never be brought about.   Although the thermal decomposition reaction may naturally be quite different from that brought about photochemically or by a-particles, it appears to me nevertheless that the relationship between the two reaction paths is worthy of remark.

PHOTOTROPIC AND PHOTOCHEMICAL CHANGES OF SOME CAMPHOR DERIVATIVES IN SOLUTION.

By Bawa Kartar Singh and Bhutnath Bhaduri.

In previous papers, [1, 2] one of us described some camphor derivatives exhibiting phototropism in solution only.   These were a-naphthylamino-d-camphor, m-phenylenebisamino-d-camphor and ar-tetrahydro-a-naphthylamino-d-camphor when dissolved in chloroform.

The phototropic change of a-naphthylamino camphor occurs also in solvents other than chloroform, namely, bromoform, ethyl alcohol solution

[1] Singh, *J. Amer. Chem. Soc.*, **43**, 333, 1921.
[2] *Ibid.*, **1**, 1924.

of iodoform and of carbon hexachloride, chloral alcoholate and methylene iodide; it is much less marked in carbon tetrachloride; but it does not at all take place in alcohol, acetone, benzene, ethylene dibromide, ethyl iodide and methyl iodide.

It is inhibited by sodium ethoxide and water in traces.

Phenomena accompanying the Phototropic Change.

(*a*) **Colour change**: The colourless solution of α-naphthylamino camphor in solvents in which the phototropic effect is observed, turns green on exposure to sunlight. The intensity of colour depends on the length of exposure. On keeping the solution in the dark, the reverse change takes place; if the exposure is very short, a nearly colourless solution is obtained but if the exposure is long, the final colour is strong yellow to yellowish red.

(*b*) The green solutions which are obtained on exposure react strongly acid to litmus, whereas solutions in which this phototropy is not exhibited, do not develop any acidity.

(*c*) In the earlier communication[2] it was found that as the colourless solution of α-naphthylaminocamphor in chloroform changed to green, the specific rotation increased to 186·6°. This point has been more carefully studied (Table I.) and it is found that the specific rotatory power of the

TABLE I.—Solvent : **Chloroform.**

	$[\alpha]_{Hg_{gr.}}$	$[\alpha]_{Hg_y.}$	Remarks on Colour Changes.
A. Concentration : 0·7502 g./100 c.c. $l = 2$ dcm.; T : 35°.			
Before exposure	138·0°	120·7°	colourless
The solution exposed for two minutes; **immediately** after exposure	138·7	121·7	green
The exposed solution kept **in the dark**—			
After 1½ hours . . .	149·3	130·6	green colour had faded
,, 3½ ,, . . .	164·6	140·6	greenish yellow
,, 5½ ,, . . .	187·9	160·0	green colour was discharged; yellow colour persisting
,, 10 ,, . . .	188·7	160·6	yellow
,, 24 ,, . . .	189·2	161·3	,,
,, 30 ,, . . .	188·7	160·6	,,
B.—Concentration : 0·7372 g./100 c.c.; $l = 2$ dcm.; T : 35°.			
Before exposure	138·6°		colourless
The solution exposed for 5 mins.; **immediately** after exposure .	139·3		green
The exposed solution kept **in the dark**—			
After 1½ hours . . .	162·8		greenish yellow
,, 2½ ,, ...	204·2		yellow
,, 18 ,, ...	204·2		,,

green solution **immediately** after exposure is almost the same but that the rotatory power of the solution increases continually attaining a maximum value when kept in the dark, which however, depends upon the conditions

of the experiment, such as time of exposure, etc. The final yellow colour of the solution indicates that in addition to the phototropic change (green colour) there is also a photochemical oxidation of α-naphthylaminocamphor to α-naphthyliminocamphor (yellow colour), and this must, necessarily, lead to increased rotatory power. This is supported by the fact that the yellow colour of the solution is discharged on shaking with zinc dust and acetic acid.

The effect of sodium ethoxide on the phototropic change as well as on the photochemical oxidation is of an inhibitory nature and is illustrated in Table II.

TABLE II.—SOLVENT : **Chloroform** (WITH A LITTLE ALCOHOLIC SOLUTION OF SODIUM ETHOXIDE).

Concentration : 0·7506 g./100 c.c. ; $l = 2$ dcm. ; $T : 35°$.

	$[\alpha]_{Hg_{gr.}}$	$[\alpha]_{Hg_{y.}}$	Remarks on Colour Changes.
Before exposure	137·9°	120·6°	colourless.
After exposure (for 5 mins.) . .	130·6	114·6	faint yellow colour.
The exposed solution kept in the dark—			
After 1 hour	131·2	114·6	„ „ „
„ 4½ hours . . .	133·2	116·6	„ „ „
„ 18 „ . . .	136·6	118·6	„ „ „
„ 42 „ . . .	136·6	118·6	„ „ „

There is a slight decrease in the rotation just after exposure ; it regains its original value when kept in the dark. There is no further increase in rotation.

In bromoform solution the colour changes are reproduced ; the rotatory power **immediately** after exposure is very slightly increased, but after several hours the green colour is replaced by yellow accompanied with a slight increase in the value of the rotatory power (Table III.).

TABLE III.—SOLVENT : **Bromoform.**

Concentration : 0·7552 g./100 c.c. ; $l = 2$ dcm. ; $T : 35°$.

	$[\alpha]_{Hg_{gr.}}$	$[\alpha]_{Hg_{y.}}$	Remarks on Colour Changes.
Before exposure	168·8°	146·4°	pale yellow due to the colour of bromoform
Exposed for 15 seconds ; **immediately** after exposure . . .	170·8	148·1	strong green
The exposed solution kept in the dark—			
After ¼ hour	170·1	147·5	green colour had distinctly faded
„ 18 hours . . .	173·5	148·8	pale yellow
The same solution was again exposed for 2 minutes . . .	174·1	149·5	strong green
The exposed solution kept in the dark—			
After 2 hours	174·8	150·2	green colour had faded
„ 5 „	174·1	149·5	very light green

In the case of iodoform, the rotatory power **immediately** after exposure is slightly lower but this value remains constant although the green colour is replaced by the original pale yellow colour (Table IV. *A*). The rotatory

TABLE IV —Solvent : Ethyl Alcohol.

	$[a]Hg_{gr.}$	$[a]Hg_{y.}$	Remarks on Colour Changes.
A. Concentration : 0·7508 g./100 c.c. iodoform added : 0·2026 g. $l = 2$ dcm. ; $T : 35°$.			
Before exposure	106·5°	93·2°	The rotation is the same as in absolute alcohol (without the addition of iodoform) ; it had a pale yellow colour
Exposed for 45 seconds ; **immediately** after exposure . . .	105·9	92·55	deep green solution
The exposed solution kept **in the dark**—			
After 2 hours . . .	105·9	92·55	green colour discharged
,, 5½ ,, ...	105·9	92·55	pale yellow (same as that of the original solution)
,, 9 ,, ...	105·9	92·55	pale yellow (same as that of the original solution)
,, 22 ,, ...	105·9	92·55	pale yellow (same as that of the original solution)
B. Concentration : 0·7506 g./100 c.c. iodoform added : 0·4014 g. $l = 2$ dcm ; $T : 35'$.			
Before exposure . . .	105·9°	92·60°	pale yellow colour
Exposed for 45 seconds ; **immediately** after exposure . .	105·9	92·60	deep green (**the colour developed was deeper than that in A**)
The exposed solution kept **in the dark**—			
After 1 hour . . .	105·9	91·94	green colour almost discharged
,, 3 hours . . .	105·9	91·26	green colour totally discharged
,, 6 ,, . . .	105·9	91·94	pale yellow colour (same as that of the original solution) persisting
,, 9½ ,, . . .	105·9	91·94	pale yellow colour (same as that of the original solution) persisting
C. Concentration : 0·7512 g./100 c.c. iodoform added : 0·4004 g. $l = 2$ dcm. ; $T : 35°$.			
Before exposure	105·9°	92·60°	pale yellow colour
Exposed for 5 minutes ; **immediately** after exposure . . .	105·2	—	deep green solution ; Hgy line could not be read
The exposed solution kept **in the dark**—			
After ¼ hour . . .	105·9	91·85	
,, ¾ ,, . . .	105·2	91·85	green colour had almost faded
,, 5 hours . . .	105·2	91·85	green colour was totally discharged
,, 18 ,, . . .	105·9	92·85	pale yellow colour

power of the alcoholic solution of the substance (even after exposure) is independent of the quantity of iodoform ; time of exposure remaining the same, the greater the quantity of iodoform added the deeper is the green tint developed on exposure to sunlight (Table IV. *B*). Even longer exposure does not effect any change of rotation of the substance in alcohol-iodoform solution (Table IV. *C*).

The order of decreasing rapidity of the colour change in the dark namely, green → colourless or pale yellow, is iodoform > bromoform > chloroform. The photochemical oxidation is most marked in chloroform, very much less so in bromoform and nil in ethyl alcohol containing iodoform.

In solvents in which the phototropic change of α-naphthyl aminocamphor does not occur, say for example, ethyl alcohol, the rotatory power of the solution **before** exposure to sunlight, **immediately** after exposure and on keeping it **in the dark** for a fairly long time (24 hours) is identical (Table V.).

TABLE V.—Solvent : Ethyl Alcohol.

Concentration : 0.7460 g./100 c.c. ; $l = 2$ dcm. ; $T = 35°$.

	$[\alpha]_{Hg_{gr.}}$	$[\alpha]_{Hg_{y.}}$	Remarks on Colour Changes.
Before exposure	$104.5°$	$89.85°$	colourless
Exposed for 5 minutes ; **immediately** after exposure . . .	104.5	89.85	,,
The exposed solution kept **in the dark**—			
After 1 hour	105.2	89.85	,,
,, 5 hours . . .	105.9	91.14	,,
,, 24 ,, ...	105.9	91.84	,,

This shows that the photochemical oxidation is absent in such solvents. In some solvents (*e.g.* chloroform) in which the observed phototropic effect is followed by rise of rotatory power (Table I.) and oxidation of the substance, it is to be assumed that the photochemical oxidation is a slow induced reaction brought about by the phototropic change which is rapid.

The Effect of Acetylation of α-**Naphthylaminocamphor on its Phototropic Behaviour.**—The **acetyl** derivative [3] of α-naphthylaminocamphor does not show phototropy in the halogen-containing solvents, namely, chloroform, bromoform, alcohol solution of iodoform and of carbon hexachloride, chloral alcoholate and methylene iodide in which the parent compound exhibits the phenomenon.

Stereoisomerism and Phototropy.—The **lævo** and **racemic** isomerides of α-naphthylaminocamhpor [3] exhibit the same colour changes on exposure as those of the **dextro** form.

Mechanism Accounting for the Colour Changes in Phototropy.—In the earlier communication,[2] it was suggested that the green colour changes may be due to the interaction of the keto and enol forms of α-naphthylaminocamphor resulting in the production of a coloured combination of the quinhydrone type. The experimental observations now recorded are also in favour of an alternative scheme. The acidity of the solution after exposure to sunlight and the fact that only those halogen-containing solvents

[3] Singh and Bhaduri, *Unpublished results.*

which contain two or three atoms of halogen attached to the same carbon atom can bring about the phototropic change may be explained on this scheme. It is assumed that a dinaphthylmethane or trinaphthylmethane derivative is first formed with the liberation of halogen acid. The methane derivative is then oxidised to the carbinol or the chloride by the action of light :

$$CHCl_3 + 3NHR \underset{R=C_8H_{14}}{\overset{CH-}{\underset{CO}{\diagdown}}} \longrightarrow CH\left[-\diagdown-NHR\right]_3 + 3HCl$$

O | light

$$HO.RHN \underset{(Cl)}{=} \diagdown === C \overset{C_{10}H_6NHR}{\underset{C_{10}H_6NHR}{\diagdown}} \underset{dark}{\overset{light}{\rightleftharpoons}} HO.C \underset{(Cl)}{\left[-\diagdown-NHR\right]}$$

Coloured   Colourless
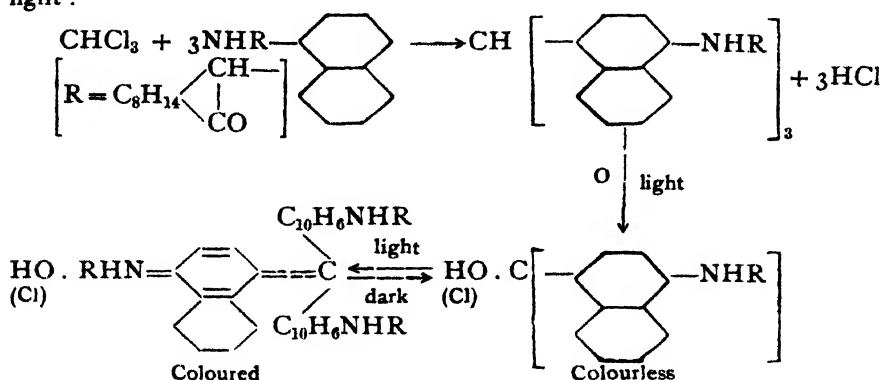
A similar explanation[4] has been offered by Lifschitz in explaining the colour changes of phototropic triphenylmethane dyes.

The inhibitory action of sodium ethoxide and water in the phototropic change can be readily understood from this scheme as these shift the above equilibrium from the coloured ionised form to the colourless unionised form of the trinaphthylmethane derivative.

Summary.

1. a-Naphthylaminocamphor shows the phtototropic effect in the following solvents which contain 2 or 3 halogen atoms attached to the same carbon atom : chloroform, bromoform, iodoform (in alcohol), carbon hexachloride (in alcohol), chloral alcoholate and methylene iodide. The exposed solutions react strongly acid to litmus. On the other hand, the effect is not shown in ethylene dibromide, ethyl iodide, methyl iodide and other ordinary organic solvents.

2. In addition to the phototropic change, there is also a photochemical oxidation of a-naphthylaminocamphor to a-naphthyliminocamphor. This photochemical oxidation is most marked in chloroform, less so in bromoform and nil in iodoform (in alcohol).

3. The photochemical oxidation is accompanied by an increase in rotation ; but as the phototropic change is not marked by any change in rotatory power it may be concluded that the new compound formed possesses the same rotatory power (which is very unlikely) or that the amount of the substance undergoing change is so small that it does not produce any alteration in rotation.

4. The phototropic colour change and the photochemical oxidation are inhibited by sodium ethoxide as well as by traces of water.

5. Acetylation destroys the phototropic effect.

6. The stereoisomeric a-naphthylaminocamphors (**d, l, dl**) exhibit identical phototropic and photochemical changes.

7. An alternative mechanism for the phototropic change of a-naphthylaminocamphor is advanced. The solvent is assumed to take part in the chemical changes involved.

[4] Lifschitz, *Ber.*, **52 (B)**, 1919, 1919-26.

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PART III. PHOTOCHEMICAL CHANGE IN LIQUID AND SOLID SYSTEMS.

INTRODUCTORY PAPER. SOME REMARKS ON SIMPLE PHOTOCHEMICAL PHENOMENA.

By Professor A. Berthoud (*Neuchâtel*).

The velocity of a photochemical reaction depends on the luminous intensity and on the concentrations of the bodies which take part in the reaction, but, if one only considers the phenomenon as a whole, the influence of these factors is not governed by general and precise laws. According to the law of Grotthus-Draper the quantity of matter transformed increases proportionally with the quantity of light absorbed. This proportionality is not, however, invariably found; thus we recognise to-day at least ten reactions of which the velocity increases proportionally with the square root of the luminous intensity. Sometimes the photochemical effect is determined simply by the quantity of light absorbed, but sometimes the concentration of the reactive body has an independent influence on the absorption. For a given quantity of light absorbed, for example, the amount of bromine which combines with cinnamic acid is proportional to its concentration. In the same way, in reactions between two bodies, the influence of the concentration of the insensitive body seems to follow no law. The quantity of matter changed by a certain quantity of light may be proportional to this concentration (*e.g.*, the action of iodine on potassium oxalate) or to its square root (*e.g.*, the formation of phosgene), or it may be independent of the concentration (*e.g.*, the action of bromine on hexahydrobenzene or cinnamic acid), or may decrease on increase of concentration (*e.g.*, the oxidation of several organic compounds by free oxygen).

By reason of this diversity in the conditions which relate the photochemical effect to the intensity of the light and to the concentrations, it follows that photochemical reactions take place in exceedingly varied manners. Light always serves to increase the internal energy of the molecules which absorb it and thus to render them chemically active; but the phenomena which follow this activation can be infinitely varied. In the first place, it is often found that a part of the activated molecules lose their energy and their activity before reacting. Other active molecules are changed, or react with further inactive molecules, and sometimes the bodies so formed are stable and the phenomenon stops there. Frequently, however, the primary reaction is followed by a more or less complex series of secondary reactions, brought about between molecules which have not been directly activated by light. The change which is then observed is the resultant of quite a series of reactions and it would thus seem that it is impossible to foretell, in each particular case, the relationships which can exist between the velocity of the reaction as a whole and the luminous intensity or the concentrations. Precise and general laws can only be applied to the simple phenomena, activation, deactivation and simple reactions. It is generally agreed that these phenomena follow the following laws :—

(1) *The number of molecules rendered chemically active by monochromatic light which gives rise to a photochemical reaction is equal to the number of quanta absorbed.* In a different form this law was announced by Starck and then by Einstein ; (it is known as the Einstein Law).

(2) *The secondary chemical reactions which are not directly influenced by light follow the law of mass action.*

(3) *The law of mass action applies also to the spontaneous deactivation of molecules ; in other words, the velocity of deactivation is proportional to the number of active molecules existing at any given moment.*

In fact, in applying these laws, we can account quite satisfactorily for the kinetics of numerous, even very complex, photochemical reactions. Certain facts, however, seem to show that these laws sometimes fall short, that they do not suffice to interpret all the observed facts, and that certain influences can intervene, of which they pay no account. On this question I propose to present a few reflections. We will concern ourselves specially with the problem of activation in its relationship with the influence of temperature, and of wavelength as well as with deactivation.

The Activation of Molecules and the Influence of Temperature on the Velocity of Photochemical Reactions.

The *so-called* Einstein law has in reality, as we know, a very different meaning from that put forward by Einstein. At first, he treated as identical the number of the activated molecules and that of the molecules changed ; he conceived, in effect, that the number of molecules of sensitive substance which enter into reaction is equal to that of the quantum absorbed. We know that this "law of equivalence" is only accurate in exceptional cases, and, in consequence, does not merit the title "law." The yields are often much greater than those foretold by the law, a fact which is explained by a series of successive reactions. They are often, too, considerably lower than expected and this is explained by a deactivation of the molecules. It is clear that when such deactivation intervenes (which can happen even when the theoretical quantum yield is exceeded) the "law of equivalence" does not apply even to the primary photochemical reaction. Does it then apply to activation? In other words, does our first law always apply exactly ?

The contrary opinion is implied in the explanation which is ordinarily given to account for the variations of the velocity of photochemical reactions with temperature or with the wavelength of the light which brings them about.

Doubtless the thermal acceleration of photochemical reactions can often be attributed to an increase of the velocity of the secondary reactions. But we must admit that increase of temperature sometimes also accelerates the primary reaction. In order to explain this acceleration it is generally assumed that molecules which have absorbed a quantum of light of stated frequency are often only activated if they already possess, before absorption, an energy greater than a certain limit.

If we represent by ϵ the critical increment, that is to say the amount of energy which must be given to a molecule (taken in the mean state) in order to render it chemically active, the thermal acceleration of the reaction taking place in the dark is given by the relationship :

$$d \ln k = \frac{N\epsilon}{RT^2} dT . \qquad . \qquad . \qquad . \qquad . \quad (1)$$

33

In order that a molecule can be brought into the active state by a quantum of light, its energy must exceed the molecular energy by at least $\epsilon - h\nu$. If the velocity is simply proportional to the concentration of the active molecules, the thermal acceleration of the photochemical reaction is thus expressed by the equation :

$$d \ln k = \frac{N(\epsilon - h\nu)dT}{RT^2} \qquad . \qquad . \qquad . \qquad (2)$$

According to this formula the thermal acceleration, as in fact is found, is weaker for a photochemical reaction than for the same reaction when carried out in the dark. It ought also to decrease with the wavelength of the light and this also has been observed.

It is clear that according to this hypothesis the number of molecules activated by light will very often be less than the number of quanta absorbed. These numbers can only be equal when the quantum yield is independent of the wavelength.

This interpretation of the thermal acceleration of photochemical reaction was proposed as long ago as 1918 by Pratolungo [1] and was then developed by Tolman.[2] It was analysed by Allmand in the paper presented to the meeting of this Society in 1925, and I myself have accepted it in my book on Photochemistry. If, however, one examines it anew, it seems to be less satisfactory than at first sight, and it would appear that the variations of the photochemical effect as a function of the wavelength of the light are, in fact, very different from those which should follow from formula (2).

In order to fix our ideas we give in Table I. (column 3) the number of molecules (in fractions of the total number) whose energy exceeds certain limits indicated in the second column, where E represents the mean molecular energy. These limiting energies are expressed in calories (column 4) for the case where the temperature equals $27°$ C.

TABLE I.*

Molecular Heats.	Limiting Energies.	Number of Molecules.	E Limit (g. cal.).
3	2·66 **E**	0·0257	2,454
	6·0 **E**	0·000156	5,400
10	2 **E**	0·051	6,000
	3 **E**	0·0028	9,000
	4 **E**	0·000031	12,000
20	2 **E**	0·0096	12,000
	3 **E**	0·000013	18,000

* The numbers relating to the molecular heat $Cv = 3$ have been calculated by means of the integrated Maxwell formula (see e.g. Jeans, " Théorie dynamique des gaz," p. 3, Paris, 1926). Those relating to molecular heats 10 and 20 are deduced from the " generalised Maxwell formula " (Berthoud, *J. Chim. physique*, 11, 577, 1913) which applies without doubt to liquids as well as to gases. The numbers relating to those molecular heats represent only a rough approximation but they are sufficiently accurate for our purpose.

In Table II., on the other hand, we give the values of the product $Nh\nu$ of the quantum by the Avogadro number, for some wavelengths :—

[1] Pratolungo, *Razz. chim. Ital.*, **48**, 121, 1928.
[2] Tolman, *J. Amer. Chem. Soc.*, **45**, 2285, 1923.

TABLE II.

800 $m\mu$	35,600 g. cal.	400 $m\mu$	71,250 g. cal.
700	40,700	300	95,000
600	47,500	250	114,000
500	57,000	200	142,500

The figures in Table I. demonstrate directly the well-known fact that molecules, whose energy much exceeds the mean, form only a very small fraction of the mass of a body. Compared with those of Table II. they demonstrate that if even a very small number of molecules possess (according to Tolman's conception) sufficient energy to be activated by a certain quantum of light, it should be sufficient to increase only slightly the frequency of the light to make all the absorbing molecules active, and, in consequence, to increase the velocity of reaction considerably. If, for example, in a substance whose molecular heat is 10, light of wavelength 400 $m\mu$ activates, at a temperature of 27° C., only those molecules whose energy is three times the mean, those with an energy twice the mean would be activated by light of 384 $m\mu$ and all the molecules would be activated by light of 355 $m\mu$. For the same number of quanta absorbed, the quantity of matter changed by light of 400, 384 and 355 $m\mu$ would vary in the same proportion as the numbers 0·0028, 0·051 and 1. For wavelengths shorter than 355 $m\mu$ the quantum yield would remain constant.

Thus, in a small spectral interval following immediately on the threshold, the velocity of reaction ought to increase very rapidly with the frequency to become then independent of the frequency.

Things do not happen this way in fact. Indeed, we have no precise information as to the increase of yield with frequency in the immediate neighbourhood of the threshold. In almost all photochemical reactions which do not follow the "law of equivalence" we find, however, in proportion as the frequency rises, a slow increase of the quantum yield in a very wide spectral zone. On the other hand, the Pratolungo-Tolman theory, according to what has been said, only permits an acceleration by the heat of a photochemical reaction when the transformation is effected under the influence of light whose frequency is but slightly greater than that which corresponds to the threshold.

We must, therefore, look for another interpretation than that of Tolman to explain the influence of wavelength and of temperature on the quantum yield.

The influence of wavelength is readily understandable. We must assume, first of all, that the activity of a molecule is of varying degrees and that the more its internal energy is increased the greater are its chances of dissociating or of reacting with other molecules. On the other hand, it is probable that (excepting the case of fluorescence) molecules which de-activate spontaneously lose their energy only gradually and give it up by small quanta to the molecules with which they collide. If that be so, a molecule which has absorbed a quantum of light just sufficient to render it active retains its activity under normal conditions for a shorter time than one which has absorbed a larger quantum. The period of the active state should therefore increase with the frequency of the light, and this should hold also with the quantum yield, so long as, in the primary reaction, it is less than unity.

This point of view makes it possible to understand how the thermal

coefficient of a photochemical reaction tends to decrease when the wave-length of the light decreases. We conceive in effect that a thermal acceleration, such as may cause it, may be so much the weaker as the molecules, which become deactivated before they react, are the fewer. If their number is nil, the primary photochemical reaction follows the " law of equivalence " and the thermal coefficient becomes equal to unity.

It appears to me, however, not impossible that an increase of frequency can also have a direct influence on the secondary reactions, or at any rate on the first of such reactions. We may imagine, for instance, that the molecules formed in the dissociation of a molecule A ought to have an energy (and in consequence a chemical activity), so much the greater as the internal energy of molecule A is higher. If that be so, an influence of the wavelength on quantum yield does not necessarily indicate, as one ordinarily supposes, that only a portion of the molecules activated by the light will enter into reaction.

If, now, we pass to the causes of the thermal acceleration, we shall notice at first that a strong acceleration is never found except in complex photochemical reactions, and this may be attributed to secondary reactions. Photochemical phenomena which may be considered as simple invariably have a small thermal coefficient. Experimental figures do not warrant the fixing of a definite limit, but it would appear not to be appreciably greater than 1·2. This small temperature influence can be attributed to many causes which, however, cannot very readily be specified. It is reasonable to suppose that the ease with which two molecules can react depends not only on their total energy but also on their individual energies, and that a molecule activated by light has so much the greater chance of reacting with another molecule as its internal energy is the higher. In addition, in a liquid medium, an increase of temperature tends to facilitate a chemical reaction by diminishing the viscosity, just as in a dark reaction.

It does not seem actually possible to analyse much further the causes of the influence of temperature or of wavelength on the velocity of photo-chemical transformations; this can only be fruitfully done when these influences have been the object of systematic researches.

We can, however, conclude from the foregoing that, apart perhaps from a narrow spectral zone in the neighbourhood of the threshold, each quantum of light capable of inducing a chemical reaction activates one molecule.

We should have been able to close this section here were it not that in a recent paper it has been suggested that a single quantum of light sometimes directly activates several molecules. The author of this paper, K. P. Basu,[3] founds his opinion on the following considerations.

The Raman phenomenon shows that a quantum of light can be absorbed only partially, while the rest is diffused. It is then possible that a quantum of sufficiently high frequency may be absorbed in three or four roughly equal fractions, and may successively activate three or four molecules. In this way the increase of quantum yield with frequency might be explained.

We wish to make a few observations on this hypothesis of Basu. In the first place, we know that we need not pay attention to the influence of wavelength on quantum yield. On the other hand, it must be stated that the part of a quantum which is absorbed in the Raman effect is invariably small and corresponds to an infra-red spectrum remote from the visible. If, as Basu would have it, the photons (or at least a proportion from among them sufficiently large to produce an appreciable influence on the quantum

[3] K. P. Basu, *J. physikal. Chem.*, **33**, 1200, 1929.

yield) were absorbed by approximately equal fractions, a ray of monochromatic light, in traversing an absorbent medium, would be split up into rations of very different wavelengths. Since this phenomenon (quite different from fluorescence) has not been observed, it seems to me that we ought not to be too much attracted to Basu's hypothesis.

Deactivation of Molecules and the Grotthus-Draper Law.

So far, we have been considering that, in a medium of a given composition, the velocity of the primary photochemical reaction is proportional to the quantity of light absorbed. In the reactions of the halogens, for instance, in which the velocities are proportional to the square root of the luminous intensity, the dissociation of the halogen molecules which constitutes the primary phenomenon follows the Grotthus-Draper law and there is no indication that it can ever do otherwise. From this we must conclude that in a medium of a given composition the number of molecules deactivated without reacting bears always a constant relationship with the number of activated molecules, *i.e.* deactivation follows the law of mass action, or in other words the velocity increases proportionally with the number of active molecules present at a given moment. In the first place it must be pointed out that this law is not equivalent to the Grotthus-Draper law applied to the primary photochemical reaction. The latter law might fail to apply without affecting the validity of the form. This would happen, for instance, if reaction took place between two molecules activated by light, for the velocity could then increase proportionally with the square of the luminous intensity. Certain photochemists consider that they have verified this proportionality between velocity and the square of the intensity in the case of certain reactions, but these observations have not been confirmed and were erroneous.[4]

If, in a medium of stated composition, the primary photochemical effect is constant in regard to a given quantity of light absorbed, a different state of affairs is found when the composition of the system is varied. Very often the quantum yield changes with the concentration of the inactive body and sometimes also with that of the active body. An example of the latter type is furnished by the polymerisation of anthracene. This reaction, however, is bimolecular and it probably is effected by the interaction of an activated and a normal molecule; for this reason the photochemical effect for a given quantity of light increases with the concentration as would be expected in accordance with the law of mass action. This case then is quite normal.

The Grotthus-Draper may sometimes break down for purely physical reasons quite different from those envisaged above.

We know that the fluorescent power of a substance in solution commences to diminish and finally vanishes when the concentration is increased. Fluorescence is equally diminished or suppressed if we add a suitably chosen substance to the solution. Fluorescent vapours give rise to analogous observations. J. Perrin,[5] who has made a special study of these phenomena, attributes them to a molecular induction of an electromagnetic

[4] I will only cite the case of the oxidation of ethyl alcohol by free oxygen in presence of benzophenone as a sensitiser, as studied by Böseken and his pupils. Measurements at present unpublished, which I have made show that in fact the velocity of this reaction is proportional simply to the luminous intensity.

[5] See especially *Réunion Internationale de Chimie physique, Activation et Structure des molécules*, p. 354, 1928.

nature by which one molecule transfers energy to another in its neighbourhood. This induction cannot take place between any two molecules whatsoever; it only takes place in general, between molecules having a certain synchronism which permits resonance. We notice in fact that a substance which extinguishes the fluorescence of a dissolved body has an absorption band coinciding roughly with the absorption band of the fluorescent body. An extinguishing action is also produced by substances, such as sulphides or iodides, which do not exhibit such an absorption band but which have a feebly bound electron in the molecule.

Several possibilities can be visualised. The energy of the molecule excited by light can transfer itself to another molecule, the internal energy of which is increased when it is activated. This phenomenon is known as *collision of the third kind*, but according to Perrin's conception it takes place between neighbouring molecules which are not necessarily in contact. An active molecule can also give up its energy to another in the form of kinetic energy and, in consequence, without activating it. This so-called *collision of the second kind* is the inverse of the non-elastic collision of the first kind in which the impact of the two molecules serves to increase internal energy of one of them and to activate it. According to J. and F. Perrin the so-called collision of the second kind should also consist in an electromagnetic induction which can only take place between synchronous molecules; this conclusion ought to be applied also to the non-elastic collision of the first kind since this represents the inverse of the collision of the second kind. Hinshelwood[6] has definitely suggested that the activation of molecules of ethyl ether or propionaldehyde is not produced by molecular impact at all. Whilst the collisions with molecules of hydrogen are activating, those with molecules of helium, nitrogen, carbon monoxide or dioxide, and methane have little or no effect.

One imagines that these molecular interactions ought to manifest themselves in different ways in photochemical changes. Certain sensitisation phenomena by fluorescent materials as well as the energy transfer from one molecule to another in chain reactions, as conceived by Christiansen, should be ascribed without doubt to collisions of the third kind. On the other hand it is obvious that deactivation of the molecules by collisions of the second kind ought to result in the slowing down or complete arrest of a photochemical reaction. The experiments of J. Perrin and Mlle. Choucroun[7] have effectively shown that the velocity of the bleaching of eosin or methylene blue in glycerin decreases, as well as the fluorescence, as the concentration is increased. It is thus reasonable to attribute certain negative catalyses of photochemical reactions (such as happens often in the case of oxygen) to a deactivation by molecular induction.

We must therefore admit that, in a given medium, the velocity of deactivation of molecules and, in consequence, the period of the active state may sometimes be pronouncedly modified by a simple change in the concentration of the sensitive body or by the addition of a small quantity of foreign matter.

At the same time this conclusion should not be generalised, and we are now face to face with a surprising fact. The diminution of fluorescence with increase of concentration is a quite general fact both for gases and for solutions. We might expect therefore that in the primary photochemical

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[6] Hinshelwood, *Proc. Roy. Soc.*, **114A**, 84, 1927; Hinshelwood and Askey, *ibid.*, **115A**, 215, 1927 and **116A**, 163, 1927.

[7] Mlle. Choucroun, *Compt. rend.*, **178**, 1407, 1924. See also Le Vaillant, *ibid.*, **177**, 398, 1923.

reaction, the quantum yield would tend always to diminish when the concentration of the substance appreciably increases. In fact nothing of the kind occurs. So far as I am aware, this diminished yield has only been noticed in reactions with an appreciably fluorescent body. In other photochemical reactions taking place in a gaseous system or in solution, the quantum yield sometimes increases with the concentration as we have seen, but never has there been any indication of a decrease in the period of the active state when the concentration of the active body is increased.

This fact, thanks to which the kinetic of photochemical phenomena are fortunately simplified, and which we are now accustomed to consider as perfectly natural, is in reality, as has already been said, very unusual and, so far as I am aware, has never been explained.

We must ask in the first place whether we cannot account for the observed facts by assuming that the concentration of the sensitive substance invariably has an influence on the period of the active state, but that this influence has no effect on the progress of the greater number of photochemical reactions. We should have to imagine, in the first place, that in most cases the primary photochemical phenomenon follows so closely upon the activation that the two phenomena are practically simultaneous and that there is no time for deactivation. This hypothesis would naturally imply that the "law of equivalence" applies almost invariably to the primary photochemical reaction—which is scarcely admissible. On the other hand according to the experiments of Stern and Volmer [8] a molecule can absorb, without becoming dissociated, a quantum of light much greater than its energy of dissociation. In fact, the existence of monomolecular reactions in a gas indicates that the number of molecules which are decomposed is not equal to the number of molecules which are activated by molecular impact. These two numbers only become equal at very low pressures, when the period between two collisions is sufficiently long.

Another hypothesis would consist in imagining that the primary photochemical reaction, like deactivation, requires the impact of an active molecule and an ordinary molecule of sensitive material of such a kind that, whatever be the concentration of the latter, the proportion between the numbers of molecules changed and of molecules deactivated remains constant. But this hypothesis reduces itself to the former one and involves the same objections in the case of all reactions which follow the "law of equivalence." Besides it is contradicted by the existence of mono-molecular reactions in the gaseous system. These reactions show, in fact, that the velocity depends simply on the number of active molecules existing at a particular moment and not on the collisions they undergo.

We must, therefore, admit that in most photochemical reactions the period of the active state is quite definitely independent of the concentration of the sensitive substance and that if the excited molecules of fluorescent bodies are deactivated by molecular induction, those of non-fluorescent bodies, as a rule, are not. Perhaps it is possible, if not to explain this difference conclusively, at any rate to indicate a direction in which a solution can be sought.

Whilst a fluorescent molecule deactivates on losing at a blow a quantity of energy scarcely equivalent to the quantum absorbed, it is reasonable to assume the deactivation of a non-fluorescent body takes place gradually by the successive loss of several small quanta. Now, if deactivation by induction requires (as we must admit it does) the same period of resonance in

[8] Stern and Volmer, *Z. Wiss. Phot.*, 19, 275, 1920.

the two molecules which take part in the phenomenon, it is natural to suppose that no interaction between an active molecule and another molecule of the same substance unless the latter is in a certain fixed condition. We must presume that if a molecule passes from state A to state A' this phenomenon can only have a resonance effect on another molecule and can only be induced by it if the latter is in one of the states A or A'. If the second molecule is in state A', there may reasonably be a collision of the third kind, or a transfer of internal energy from the first molecule to the second. If it is in state A we should expect, rather, a collision of the second kind, with deactivation of one at least of the two molecules. Now, in the deactivation of a fluorescent body A' represents a normal condition to which a large number of the molecules of the body in question are to be found. In these conditions there is a considerable chance of induction taking place. In the case of a non-fluorescent body, the first states A', A″ (through which the deactivating molecule passes by corresponding degrees) has a much higher energy than the mean value, and these states, in consequence, are scarcely to be found in the molecules which have not been subjected to the action of light. One imagines, in consequence, that the ordinary molecules of the sensitive substance will have no appreciable effect on deactivation.

It is clear that we have only sketched a simplified and very incomplete scheme, but this interpretation seems to me to follow logically from the ideas of Perrin on molecular induction. If it is true we may expect that induced deactivation would manifest itself sometimes in photochemical reactions between non-fluorescent bodies, and more reasonably in those which are accompanied by a thermal reaction which takes place in the same fashion. An examination of the more certain experimental figures relating to the velocity of photochemical reactions would perhaps lead to interesting conclusions on this subject. It happens quite often that the *progress of a reaction only approximately follows the laws by which we have sought to foretell the steps of the reaction in order to account for the facts.* These variations are normally attributed to hypothetical reactions of secondary importance. It is by no means impossible that they may sometimes be attributed to influences such as those we have just discussed.

To sum up. The Grotthus-Draper law applies almost invariably within the limit of experimental error if we vary the concentration of the sensitive body, but this fact (which is generally considered as more or less self-sufficient) has, in truth, in accordance with the present views as to deactivation, received little attention. I desire, above all, to draw attention to this point.

GENERAL DISCUSSION.

Professor A. J. Allmand (*London*) said : I would wish to say how grateful all photochemists working with solutions will be to Professor Berthoud for his lucid and very individual, though impersonal, introduction to the subject, as also for delivering it in a manner which made it so easy to follow. Professor Berthoud disclaimed at the outset any attempt to offer definite solutions of the two main problems on which he has focussed attention. There is no doubt that fruitful discussion of photochemical reactions in liquid media is bound to remain in arrears of experimental work until our interpretation of the absorption spectra of solutions has advanced considerably and until the kinetic theory can be applied more satisfactorily to such systems.

THE PHOTOCHEMICAL TEMPERATURE COEFFICIENT.

BY K. W. YOUNG AND D. W. G. STYLE.

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1. Since Goldberg[1] first pointed out the low values generally obtained for the photochemical temperature coefficient several papers on this subject have appeared,[2] in which attempts have been made to give a theoretical or empirical interpretation of them. When the reaction is one taking place in the gas phase, success has often been attained and the significance of the temperature coefficient completely determined (*e.g.* the combination of hydrogen and bromine).[3] In liquid systems, however, the conditions are more complex, and not infrequently the coefficients are very large and their explanation a matter of some difficulty, the more so because in many cases the temperature effect arises from several independent causes. (See § 2.)

In the present communication, possible sources of the influence of temperature will be considered, especially those applicable to reactions occurring in solutions, which could give rise to temperature coefficients which are functions of concentration, wavelength or of temperature in a manner which differs from that to be expected from the Arrhenius relation.

$$\frac{d \ln \gamma}{dT} = \frac{E}{RT^2}$$

It is perhaps unnecessary to add that unless the opposite is stated the temperature coefficients employed will be those of the quantum yield and not those of the reaction velocity.[4]

2. The main factors which could produce a temperature coefficient are :—

(i) Dependence of deactivation efficiency upon temperature.

(ii) Dependence on temperature of the probability of the dissociation upon collision of a molecule which has absorbed a quantum greater than the heat of dissociation into two normal atoms or radicals.

(iii) The supplying from thermal sources of the energy deficiency, when the absorbed quantum is not large enough to produce a chemically active molecule.

(iv) The physical equilibria between the various energy levels of the absorbing molecule.

(v) The dependence of the predissociation limit upon temperature, if the light used covers a considerable range of frequencies.

(vi) The necessity of thermal activation at some stage in the process succeeding the light absorption.

[1] Goldberg, *Z. physik. Chem.*, 41, 1, 1903.

[2] Plotnikow, *ibid.*, 78, 573, 1911; Berthelot, *Comptes rend.*, 160, 440, 1914; Bancroft and Allen, *Proc. Nat. Acad. Sci.*, 15, 445, 1929; Tolman, *J.A.C.S.*, 42, 2506, 1920, and 45, 2285, 1923; and numerous papers by Dhar and his co-workers in the *Journal of the Indian Chemical Society* and elsewhere.

[3] *Z. physik. Chem.*, 121, 127, 1926.

[4] For a discussion of this point see, for example, Griffith and McKeown, " Photo-processes in Gaseous and Liquid Systems," p. 651 (Longmans, 1929).

(vii) Dependence of the extinction coefficient upon temperature.

(viii) Diffusion and convection.

(ix) Chemical equilibria accompanied by an appreciable heat effect.

The very slight dependence of the intensity of fluorescence upon temperature suggest that a coefficient due to (i) will be small, and apart from the increase in the collision number with rising temperature (ii) can probably also be neglected.

A considerable coefficient showing marked dependence upon wavelength might be produced by (iii). The importance of this process is, however, probably small.

Tolman [5] has deduced expressions for the temperature coefficient of a photochemical reaction and the dependence of the coefficient upon wavelength, for the case in which only the higher vibrational levels of the absorbing molecule become chemically activated by light. His expressions would, however, only be applicable to an idealised substance, since they take no account of the variation of the extinction coefficient with the energy content of the molecule and the wavelength. Wulf,[6] has attacked the problem from a more practical standpoint, and by making certain assumptions as to the relative extinction coefficients of chlorine gas in the green region of the spectrum has calculated a value for the temperature coefficient of the photocombination of hydrogen and chlorine which, when the new numbering of the vibrational levels of chlorine [7] is used, agrees fairly well with the experimental value obtained by Padoa.[8] Padoa, however, finds a coefficient of $1 \cdot 17$ in long wavelength ultra-violet light, and although there is a considerable divergence of opinion as to the temperature coefficient of this reaction,[9] thermal activation is apparently necessary for the propagation of the chain. If we take Padoa's figure of $1 \cdot 17$ as representing the temperature coefficient of the chain process and correct the coefficient for green light accordingly, the agreement between the experimental and calculated values is destroyed. The discrepancy may be due to experimental error or possibly to the neglecting of the occurrence of dissociation upon collision, a factor which will, however, be of less importance in reactions involving chlorine than with the other halogens owing to the small excitation energy of the $^2P_{3/2}$ chlorine atom. The temperature coefficient in the green would according to Wulf be almost entirely that of the extinction coefficient and not of the quantum yield.

An expression which would give the value of the temperature coefficient (when dissociation upon collision may be neglected) arising in this way, is

$$\frac{d \ln \gamma}{dT} = \frac{d}{dT}\left(\ln\left\{ \frac{\Sigma a_c N_c}{\Sigma a_c N_c + \Sigma a_D N_D} \right\} \right)$$

where N_c is the concentration of some energy level whose continuum starts to the long wavelength side of the wavelength used, and N_D the concentration of a level whose continuum starts to the short wavelength side of this wavelength. $a_c{}'$ and a_D are the corresponding extinction coefficients and γ the quantum yield, the summations being carried out over all the appropriate levels.

[5] Tolman, *J.A.C.S.*, **42**, 2506, 1920, and **45**, 2285, 1923.

[6] Wulf, *Proc. Nat. Acad. Sci.*, **16**, 27, 1930.

[7] Elliott, *Proc. Roy. Soc.*, **A127**, 638, 1929.

[8] Padoa, *Atti. Accad. Lincei*, **25**, 215, 1916.

[9] Bodenstein and Unger : *Z. physik. Chem.*, **B 11**, 253, 1930 ; Lind and Livingstone, *J.A.C.S.*, **52**, 593, 1930.

When a fairly broad band of wavelengths is employed for a photo-chemical investigation and the spectrum of the absorbing molecule is of the predissociation type, the shift of the predissociation limit[10] towards longer wavelengths with rising temperature would produce a temperature coefficient depending, however, markedly upon the breadth of the spectral region employed.

3. Excepting the last, the remaining factors to be considered are those which affect the length of the chain which succeeds the direct photo process.

Thermal activation will always be needed when a link of the chain is endothermic, and in magnitude will be at least equal to the heat absorbed. Even when the link is exothermic, activation may be necessary.[11]

Reactions in which the rate of reaction is proportional to the square root of the intensity, i.e., in which the rate of disruption of the chains is proportional to the square of the "catalyst" concentration, will have a rate dependent upon the concentration of the absorbed quanta,[12] and consequently changes in the extinction coefficient will produce a temperature coefficient of the quantum yield, which in the ideal case would be equal to that of the square root of the reciprocal of the extinction coefficient. The actual magnitude may, however, be considerably modified, especially when the extinction is large, by diffusion and convection, the effects of which will now be considered.

Plotnikow[13] has suggested that diffusion might produce an appreciable temperature coefficient in solution. The existence of some such effect (albeit rather different from that envisaged by Plotnikow) has been found in the oxidation of potassium oxalate by iodine. For this reaction Berthoud and Bellenot[14] find the temperature coefficients for 10° between 25° and 40° to be 3·22 and 3·15 in red and blue light respectively. These values have been confirmed for the same mean temperature, as shown in Table I., which shows that the coefficient is at a minimum in the neighbourhood of 579 $\mu\mu$.

TABLE I.

$[I_2] = 0\cdot00256\ M$; $[KI] = 0\cdot01018\ M$; $[K_2C_2O_4] = 0\cdot7595\ M$.

$\lambda\mu\mu$	365	405	436	546	579	675
T.C.	4·86	3·56	3·40	3·06	2·80	3·18

The extinction of the solution for the shorter wavelengths was very high and it was observed that after the reaction had been in progress for some time, the front portion of the solution was practically colourless while the rear portion was still deeply coloured, there being a fairly sharp line of demarcation between the two regions. The reaction was thus taking place in a region where the concentration gradient of both molecular and atomic iodine was large. The effect upon the temperature coefficient of reducing these concentration gradients by stirring the solution with a small glass stirrer is shown in Table II.

Under the heading "stirring" is given the revolutions per minute of the stirrer.

It is thus evident that a large fraction of the temperature coefficient for the shorter wavelengths is eliminated by the reduction of the concentration

[10] Henri, Trans. Far. Soc., 25, 765, 1929.
[11] Eyring and Polanyi, Naturwiss., 18, 914, 1930; Franck and Rabinowitsch, Z. Elektrochem, 36, 794, 1930.
[12] Allmand, J. Chem. Soc., 1557, 1929.
[13] Plotnikow, Lehrbuch der Photo Chemie.
[14] Berthoud and Bellenot, J. Chim. Physique, 21, 308, 1924.

gradients by stirring. This would appear to be due to this reaction being one in which the rate is proportional to the square root of the intensity, *i.e.* one in which the quantum yield depends inversely upon the concentration of the iodine atoms produced by light. In unstirred solutions the diffusion and convection will tend to reduce the concentration gradients mentioned above and therefore the concentration of atomic iodine. Elevation of the temperature will increase the influence of these factors and consequently raise the quantum yield.

It is difficult to decide whether more efficient stirring would still further reduce the temperature coefficient for 365 $\mu\mu$, but it is not improbable that it would and that in the complete absence of diffusion and convection effects the temperature coefficients for all wavelengths below about 580 $\mu\mu$ would be the same, *i.e.* 2·8-3·0.

The cause of this residual temperature coefficient is as yet uncertain.

TABLE II.

$\lambda_{\mu\mu}$.	Stirring.	T.C.
365	None	4·96
365	30 r/m	3·77
365	300 ,,	3·10
436	None	3·40
436	300 r/m	2·77
546	None	3·06
546	300 r/m	2·92

Of the sources of temperature coefficient so far considered (iii), (iv) and (vi) will give rise to coefficients of the Arrhenius type. A dependence upon the wavelength will occur with (iii), (iv) and (v) and, in so far as the extinction coefficient depends upon wavelength, also in (viii). A slow rise of temperature coefficient over a wide range of wavelengths would, however, be improbable with any of these and unless (i) is accepted as the cause of such results as those given in Table VI., there must be operative some other factor as yet unconsidered. Table VI. also exhibits what may be termed the normal reciprocal relationship between the quantum yields and the temperature coefficients with changing wavelength. Exceptions may occur, as for example the decomposition of hydrogen peroxide [15] when the quantum yield is not independent of the intensity, on account of the change of extinction coefficient.

The temperature coefficient should also be independent of the concentration of the reactants.

4. For relatively few reactions has the effect of temperature upon the quantum yield been investigated over a wide range of conditions, but of those which have been, a rather large proportion show exceptional behaviour, either with respect to temperature, concentrations or wavelength.

To explain the temperature anomaly branching chains or a change in the stability of some intermediate product with temperature, have been suggested.

The quantum yield of the ammonia sensitised combination of hydrogen and oxygen [16] shows only a slow increase with temperature below 405° C., but between 405° and 415° the temperature coefficient increases exceed-

[15] Allmand and Style, *J. Chem. Soc.*, 596, 1930.
[16] Farkas, Harber and Harteck, *Z. Electrochem.*, **36**, 711, 1930.

ingly rapidly with temperature, and at the upper temperature explosion sets in.

This change is supposedly due to a transition from the exothermic processes

$$H_2 + O_2 + H \rightarrow OH + H_2O \qquad . \qquad . \qquad . \quad (a)$$

$$OH + H_2 \rightarrow H_2O + H \qquad . \qquad . \qquad . \quad (b)$$
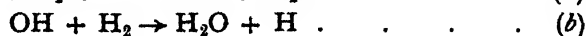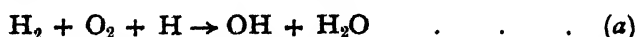
which cause the reaction below 405°, to a mechanism in which (a) is replaced by

$$H_2 + O_2 + H \rightarrow 2OH + H - 14 \text{ Cal.} \qquad . \qquad . \quad (c)$$

which, being endothermic will, excepting at the higher temperatures, be negligible compared with (a). As soon, however, as temperatures are attained at which (c) occurs with an appreciable frequency, the fact that besides perpetuating the original chain it generates two new ones, will cause a very marked increase in the reaction rate, which will rise very rapidly with temperature until finally, every chain branches according to (c) and an infinite quantum yield and explosion will result.

The temperature coefficients of reactions in which similar changes to these occur will have values given by the expression obtained by differentiating the expression

$$\gamma = I_0 A e^{-\frac{Q_1}{RT}} \left(1 + B e^{-\frac{Q_2}{RT}} \right).$$

This type of temperature coefficient is discussed by Kistiakowski[17] and Semenoff.[18]

A branching chain mechanism could also be called upon to explain the temperature coefficients of the bromine sensitised transformations of maleic acid and its esters into the fumaric isomers, whose temperature coefficients increase with temperature over the whole range of temperatures at which measurements have been made (5°-25° C.), the increase becoming very rapid for temperatures above 20° C.

Such a mechanism would be more in line with general experience than Wachholtz's[19] assumption that a new degree of freedom in an intermediate substance becomes operative at about 20° C. whereby the stability of the substance is increased and the chains lengthened.

Another possible explanation is suggested by analogy with gaseous reactions in which a transition from a heterogeneous reaction of low activation energy to a homogeneous one needing higher activation takes place. Such a change from a low activation process to one of high activation would be possible if the chain length of the high activation reaction were much the greater or if the conditions capable of producing reaction after the higher activation were far more frequent of occurrence than those favourable for the low activation reaction. Such might be the case, for example, if the reaction at low temperatures were due entirely to molecules of bromine, which were not "solvated" by ester or acid molecules, while at the higher temperatures reaction of the solvated bromine molecules became possible. Evidence that such solvation occurs has been found by Schmidt.[20] The experimental data are confined to too narrow temperature limits for definite conclusions to be drawn as to the true cause of the exceptional behaviour of these reactions.

[17] Kistiakowski, *Proc. Nat. Acad. Sci.*, 15, 194, 1929.
[18] Semenoff, *Z. physik. Chem.*, B2, 161.
[19] Wachholtz, *ibid*, 125, 1, 1927.   [20] Schmidt, *ibid.*, B1, 205, 192 .

5. The temperature coefficients of most gaseous photochemical reactions. is small, lying usually between 0·8 and 1·4. This is indeed to be expected for those which occur at a measurable rate.

The ratio of the rates of a photochemical and thermal reaction, both of which require the same activation energy and proceed by the same mechanism, will be roughly given by

$$\frac{\text{number of quanta absorbed per c.cm.}}{\text{total number of molecular collisions per c.cm.}},$$

which will normally be less than 10^{-8}.

Since the temperature coefficients of thermal gaseous reactions measurable at room temperature lie between 2 and 3, a very much smaller value is to be anticipated for photochemical change.

In solutions, however, the temperature coefficients of both thermal and photochemical reactions are often much higher, the increase being especially large for photochemical reactions, values of 3 and more having been observed. It does not appear entirely probable that such high temperature coefficients represent true energies of activation.

An effect of solvation upon the quantum yield has already been suggested by Schmidt,[20] who showed that there was a decrease in the extinction of solutions of bromine in carbon tetrachloride upon the addition of maleic ester. Since Wachholtz[21] found that each quantum of light transformed only about $\frac{1}{25}$ as many ester molecules as a chemically produced bromine atom, we may conclude that the complex between bromine and the maleic ester is less photosensitive than a free bromine molecule.

The temperature coefficients produced by the formation of such complexes or solvates will, if their photosensitivity is very small and the extent of the solvation is large, be of the Arrhenius type, but owing to the occurrence of the constant, C, in the expression for the equilibrium constant, K, for the solvation process,

$$K = Ce^{\frac{Q}{RT}}$$

Q being the heat of formation of the solvate, the rate of reaction can be enormously greater than would be expected if the influence of temperature were due to Arrhenius activation.

In general temperature coefficients caused by equilibria will depend upon the concentration of the reactants, and possibly upon the wavelength of the incident radiation.

There are relatively few reactions capable of being used as a test of the importance of the equilibrium temperature coefficients. The bromination of benzene studied by Meidinger would, however, seem to provide a clear example.[22] The temperature coefficient of this reaction depends upon the concentration of the benzene, when diluted with carbon tetrachloride, as shown in Table III., in which [C_6H_6] gives the fraction by volume of benzene in the solution.

The temperature coefficients are for the temperature interval 20°-30° and for the wavelength 436 $\mu\mu$. The value 1·22 for [C_6H_6] = 0·0333 given by Meidinger is obviously in error and we will use the value 1·28 obtained from his quantum yields at 20° and 35° (0·9 and 1·4 respectively).

The disappearance of the temperature coefficient as the benzene concentration approaches zero indicates the absence of any activation for the chain process.

[21] Wachholtz, *Z. Elektrochem.*, **33**, 545, 1927.
[22] Meidinger, *Z. physik. Chem.*, **B5**, 29, 1929.

TABLE III.

[C_6H_6] . .	1	1·0	0·05	0·0333	0·02	0·01
T.C. . . .	1·61	1·47	1·41	1·22 (1·28)	1·20	1·00
$\dfrac{d\ln\gamma}{dT}$ . .	0·049	0·039	0·035	(0·025)	0·0184	0·000

The marked differences between the absorption spectra of bromine in benzene and carbon tetrachloride show that considerable solvation is occurring in benzene solution. This solvate we will assume to be $C_6H_6 . Br_2$ and its heat of formation Q calories, whence

$$K = \frac{[C_6H_6 . Br_2]}{[C_6H_6] \times [Br_2]} = Ce^{\frac{Q}{RT}}$$

C being a constant, or putting

$$[Br_2] = x, \quad [Br_2] + [C_6H_6 . Br_2] = A, \quad \text{and} \quad [C_6H_6] = B,$$

$$K = \frac{A - x}{B . x} = Ce^{\frac{Q}{RT}}.$$

If now, only light absorbed by unsolvated bromine is capable of producing bromine atoms, the fraction of the absorbed radiant energy which is chemically utilised is,

$$\frac{a_x x}{a_x x + a_{A-x}(A - x)} = \frac{1}{1 + \beta BK} \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where $\beta = \frac{a_{A-x}}{a x}$, and a_{A-x} and a_x are respectively the extinction coefficients of the solvated bromine and of free bromine.

From data obtained by Mr. Ridyard of this laboratory (who is investigating this reaction further), β for the green mercury line, 546 $\mu\mu$ and probably also for the blue line at 436 $\mu\mu$ is close to unity, if the extinction coefficients in carbon tetrachloride solution are used for those of the unsolvated bromine. As a first approximation we may therefore put $\beta = 1$. By the differentiation of the logarithm of (1) with respect to temperature we obtain the temperature coefficient per one degree of the quantum yield.

$$\frac{d\ln\gamma}{dT} = \frac{Q}{RT^2} \frac{KB}{1 + KB}.$$

From this expression and the data of Table III. the value of K and Q can be determined.

Table IV. shows the values K obtained from the various possible pairs of Table III.

TABLE IV.

B.	1·0.	0·1	0·05.	0·0333.	0·02.
0·1	36·1	—	—	—	—
0·05	47·2	71·4	—	—	—
0·0333	29·5	25·0	5·0	—	—
0·02	28·7	25·2	13·3	25·8	—
Q. (Cal.)	9·0	9·5	10·6	9·2	9·0

Neglecting those values obtained from the coefficient for $B = 0\cdot05$ the mean value of K is $28\cdot4$.

Substituting this value of K in (2) we obtain the values for Q shown in the last row of Table IV., the mean value of which (neglecting the figure for $B = 0\cdot05$) is $9\cdot2$ Cal.

The equilibrium constant thus obtained is for the temperature $25°$.

Meidinger also gives a list of quantum yields obtained at $20°$ over a wide range of benzene concentrations. If as would appear plausible we assume the quantum yields at different benzene concentrations to be given by

$$\gamma = k[C_6H_6] \times [\text{energy absorbed by free bromine}]$$
$$= \frac{kB}{1 + BK_{20}},$$

values for K_{20} can be calculated from these quantum yields. The results together with Meidinger's figures are given in Table V.

TABLE V.

B	$1\cdot00$	$0\cdot50$	$0\cdot20$	$0\cdot0909$	$0\cdot0323$	$0\cdot0196$	$0\cdot0099$	$0\cdot005$	$0\cdot0025$	$0\cdot001$	$0\cdot0002$
γ	$5\cdot4$	$3\cdot8$	$2\cdot85$	$1\cdot8$	$1\cdot2$	$0\cdot75$	$0\cdot4$	$0\cdot17$	$0\cdot11$	$0\cdot05$	$0\cdot01$
K_{20}	$8\cdot26$	$11\cdot2$	$12\cdot6$	$16\cdot8$	$10\cdot7$	$15\cdot6$	$15\cdot1$	94	16	—	—

k was taken as 50. K is obviously decreasing at the higher concentrations, but the lower ones give a mean value of about 15, while reduction to $20°$ of the K calculated from the temperature coefficient leads to $K_{20} = 36\cdot6$.

The expressions obtained if any other formula than $C_6H_6 . Br_2$ is assumed for the solvate do not yield a constant value of the equilibrium constant.

A fuller investigation of the temperature coefficient of the bromine sensitised maleic acid and ester transformations might give valuable information as to the true cause of the effect of temperature upon these reactions.

6. One further reaction whose temperature coefficient will be dealt with in detail here is the photo-decomposition of potassium ferri-oxalate, whose quantum yields have been measured by Allmand and Webb.[23] These authors found that within their limits the yield was independent of the ferri-oxalate concentration and the intensity, and concluded that the maximum possible value of the quantum yield was two.

In the present work the quantum yields have been determined at $22°$ and $52°$ for the wavelengths 436, 405 and 365 $\mu\mu$ and the temperature coefficient only, for 313 $\mu\mu$. The yields are all lower than those obtained by Allmand and Webb, but the difference probably does not exceed the rather large experimental error.

TABLE VI.

$\lambda_{\mu\mu}$.	$\gamma_{\text{A and W}}$.	γ_{new}.	γ_{mean}.	Temp. Coef.	$\frac{d \ln \gamma}{dT}$.	$\frac{2-\gamma}{2}$.	$\frac{E}{RT}$.
436	$0\cdot89$	$0\cdot81$	$0\cdot85$	$1\cdot06$	$0\cdot0058$	$0\cdot575$	$1\cdot01$
405	$0\cdot91$	$0\cdot86$	$0\cdot885$	$1\cdot057$	$0\cdot0055$	$0\cdot56$	$0\cdot98$
365	$1\cdot16$	$1\cdot05$	$1\cdot105$	$1\cdot039$	$0\cdot0038$	$0\cdot45$	$0\cdot84$
313	$1\cdot59$	—	$(1\cdot59)$	$1\cdot029$	$0\cdot0029$	$0\cdot205$	$1\cdot41$

[23] Allmand and Webb, *J. Chem. Soc.*, 1518, 1929.

The first five columns of Table VI. give the experimental data for the four wavelengths used.

Assuming with Allmand and Webb that the maximum quantum yield obtainable is 2 the lower yields actually observed could be explained as being due to deactivation of some photo-excited molecules before they can react, and the temperature coefficient to the necessity of thermal activation of the non-photo-excited partner of the reaction.

If then τ is the mean life of the excited molecule, E the thermal activation energy and t the mean time interval between collisions of two ferri-oxalate molecules, we find that

$$\gamma = \frac{2}{1 + \frac{t}{\tau}e^{-\frac{E}{RT}}}$$

$$\therefore \frac{d \ln \gamma}{dT} = \frac{E}{RT^2} \cdot \frac{1}{1 + \frac{\tau}{t}e^{\frac{E}{RT}}} = \frac{E}{RT^2} \cdot \frac{2-\gamma}{2},$$

whence the value of $\frac{E}{RT^2}$ can be calculated if the quantum yields and temperature coefficients are known.

Columns 6, 7, and 8 of Table VI. give the values of γ_{mean} used for these calculations, $\frac{2-\gamma}{2}$ and $\frac{E}{RT^2}$ from which it will be observed that $\frac{E}{RT^2}$ is practically independent of wavelength, the average being $1 \cdot 06$. This gives for E the value 2040 cals.

The above expression for γ would necessitate a dependence of γ upon t and therefore upon the ferri-oxalate concentration in contradiction to the observations. A similar expression can, however, be deduced which avoids this difficulty, if it be assumed that the temperature coefficient is due not to activation but to the presence of an equilibrium between active and inactive forms of the ferri-oxalate molecule, and that only light absorbed by the active form is effective.

$$\text{FeOx}_{\text{inact.}} \rightleftarrows \text{FeOx}_{\text{act.}} - E \text{ cals.}$$

$$\therefore \frac{[\text{FeOx}]_{\text{act.}}}{[\text{FeOx}]_{\text{inact.}}} = Ce^{-\frac{E}{RT}} = K$$

and

$$\gamma = \frac{2a_A[\text{FeOx}]_{\text{act.}}}{a_A[\text{FeOx}]_{\text{act.}} + a_I[\text{FeOx}]_{\text{inact.}}},$$

where $[\text{FeOx}]_{\text{act.}}$ and $[\text{FeOx}]_{\text{inact.}}$ are the concentrations of the active and inactive forms and a_A and a_I the respective extinction coefficients.

Putting

$$\frac{a_I}{a_A} = \beta,$$

we have

$$\gamma = \frac{2}{1 + \frac{\beta}{K}}.$$

whence

$$\frac{K}{\beta} = \frac{\gamma}{2-\gamma}$$

and

$$\frac{d \ln \gamma}{dT} = \frac{E}{RT^2} \cdot \frac{2-\gamma}{2}.$$

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It would not appear possible with the available data to decide wherein lies the difference between the active and inactive forms of the ferri-oxalate, isomeric change, dissociation, solvation, and a difference in energy level all being plausible explanations. β is a function of wavelength and it was hoped that the change in the extinction coefficient with temperature would enable K to be evaluated. The extinction coefficients at $22°$ and $52°$, together with their ratios, are given in Table VII.

TABLE VII.

$\lambda_{\mu\mu}$.	436.	405.	365.
$a_{22°}$	20·5	121	720
$a_{52°}$	26·6	145	720
$\dfrac{a_{52°}}{a_{22°}}$	1·29	1·20	1·00

If now both forms of the ferri-oxalate molecule are in the ground state so that their extinction coefficients are independent of temperature, it is easy to show that $a_{52°}/a_{22°}$ cannot be greater than $\dfrac{K_{52}}{K_{22}}$, *i.e.* $1·42$.

The absence of a dependence of a_{365} upon temperature suggests that β for this wavelength is unity whence $K_{22°}$ is calculated to be $1·24$ and K_{52} to be $1·70$.

Since $\dfrac{a_{52}}{a_{22}}$ is given in terms of K_{52}, K_{22} and β by

$$\frac{a_{52}}{a_{22}} = \left(\frac{K_{52} + \beta}{K_{22} + \beta}\right)\left(\frac{1 + K_{22}}{1 + K_{52}}\right)$$

$$= (1 + 0·21\,\gamma)\left(\frac{1 + K_{22}}{1 + K_{52}}\right)$$

we should, on rearranging and substituting for the known quantities, be able to calculate K from the absorption measurements. We find, however, that for $436\ \mu\mu$

$$\frac{a_{52}}{a_{22}} = 1·29 = (1 + 0·885 \times 0·21)\left(\frac{1 + K_{22}}{1 + K_{52}}\right)$$

$$= 1·18\left(\frac{1 + K_{22}}{1 + K_{52}}\right)$$

and an equally impossible result for $405\ \mu\mu$.

The whole discussion being highly speculative it seems best to leave the cause of this discrepancy open.

One further point of interest in this reaction which might be mentioned is the effect of mixed light upon the temperature coefficient.

Allmand and Webb have already shown that the yield is higher when spectrally impure light is employed. This has been confirmed and in addition it has been found that with mixed light the temperature coefficient may be less than unity. Thus when using a filter the light transmitted by which was composed (in energy units) of 90 per cent. $365\ \mu\mu$ and 10 per cent. $405\ \mu\mu$ a quantum yield of $1·63$ was obtained, and the temperature coefficient was $0·96$. This reduction of the quantum yield for mixed light at higher temperatures may probably be ascribed to the dependence of the extinction coefficient for $405\ \mu\mu$ upon temperature, although the connection remains rather obscure. The result seems, however, to be worth mention-

ing as it further stresses the importance of using monochromatic light for the determination of temperature coefficients.

7. Of the numerous other reactions whose temperature coefficients might be considered, mention will be made only of two with which the authors are familiar, the decomposition of chlorine water and the decomposition of hydrogen peroxide.

In the first of these, chemical equilibria will certainly play a part, and may be the cause of a considerable fraction, if not the whole, of the temperature coefficient, since both the quantum yield and the influence of temperature upon it, have been found to be very sensitive to the addition of hydrochloric acid and, in addition, it is probable that the chlorine molecules are hydrated to a considerable extent. The mechanism of this reaction being as yet uncertain, further discussion is impossible.

Risse [24] has found that the temperature coefficient of the decomposition of hydrogen peroxide by X-rays is 1·00. As the mechanism of the X-ray reaction would appear to be the same as that in light, we may conclude that the photo-temperature coefficient is entirely associated with the light absorption process and therefore probably explicable on a similar basis to that we have used for the bromination of benzene.

Our object in considering these equilibrium temperature coefficients at such length has been to emphasise the probable high importance of chemical equilibria, in particular those between a solvated and unsolvated molecule, in deciding the rates of photochemical reactions in solution.

How far solvation may influence the rates of ordinary thermal reactions in solution, it is not possible to say, but the influence of the solvent upon the rate of reaction suggests that the influence is considerable.

To conclude, the photochemical temperature coefficient is capable of giving valuable information concerning the mechanism of the reaction and also of the state of dissolved molecules, provided that a sufficiently thorough investigation of the effect of temperature is undertaken. If its full significance is to be determined, the dependence of the coefficient upon concentration, temperature and wavelength and its relation to the quantum yield must be studied with monochromatic light. Under certain circumstances the results obtained without observing these conditions not only fail to attain their purpose but may even be actually misleading.

We desire to take this opportunity to express our gratitude to Professor A. J. Allmand for his interest and assistance, and one of us (K. W. Y.) to acknowledge the receipt of a grant from the Department of Scientific and Industrial Research while a student in training.

[24] Risse, Z. physik. Chem., A140, 133, 1929.

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GENERAL DISCUSSION.

Dr. J. Y. Macdonald (*St. Andrews*) said : With regard to the paper of Young and Style on temperature coefficients, I should like to call attention to the decomposition of nitrous oxide which I investigated some time ago [1] It was necessary to use certain approximations in calculating the temperature

[1] *J. Chem. Soc.*, 1, 1928.

coefficient of that reaction, and the evidence was, therefore, not entirely satisfactory, but it seemed to point definitely to the conclusion that the quantum efficiency was independent of temperature, while the absorption of light increased 1·4 times for a 10° rise.   In view of the difficulty of reconciling this result with theory, I think that the point should be re-investigated, direct measurements of the light absorbed being made at different temperatures.

It should be noted that if it is really the efficiency which varies with temperature, then the agreement of the value of this with the stoichiometric equation and the results of Gedye [this meeting] must be put down to coincidence.

Professor Mecke said : A possible way of explaining a high temperature coefficient of a photochemical reaction is shown in Fig. 1 (case I) of my introductory paper.   Ordinary unexcited molecules will vibrate only near the minimum of the lower potential curve of Fig. 1.   But being excited by light absorption they may gain high vibrational energy, sometimes even sufficiently high to dissociate the molecule.   Now if we imagine a steep drop of the upper potential curve, a *small* change in the distribution of vibrational energy in the *lower* state (corresponding to a small change of temperature), may give rise to a *large* change in the *upper* state, thus resulting a high temperature coefficient of a photochemical reaction.

Dr. Style, in reply, said : I think that Professor Mecke is mistaken in suggesting that the shapes of the potential energy-nuclear separation curves will have any influence upon the temperature coefficient in monochromatic light, excepting in so far as the extinction coefficient depends upon them and the temperature coefficient is a function of the extinction coefficient.   The accompanying diagram may make this clear.
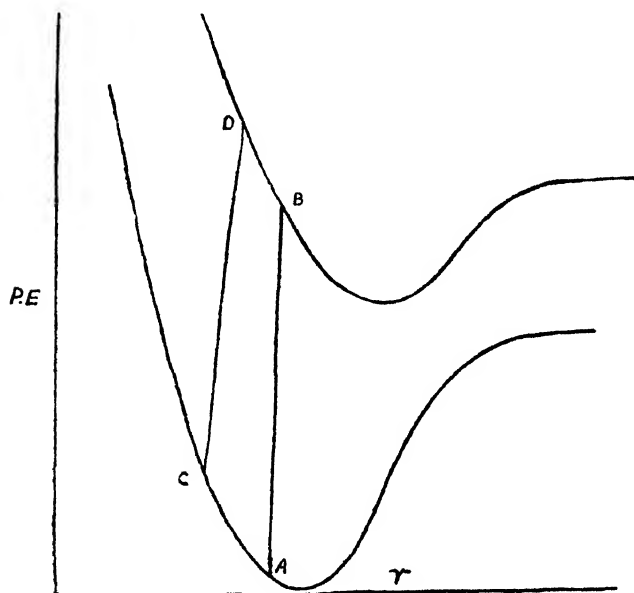
Quanta of frequency ν will raise a molecule initially in the state represented by A to the point B on the upper curve.   If, however, the molecule were initially in some higher vibrational level C, the same quantum would raise it to the point D on the upper curve, from which the molecule can dissociate.   The projections of AB and CD upon the P.E. axis will be equal since they represent equal energy increments, but they will not in general be parallel to this axis.   The resultant temperature coefficient is obtainable from the expression on page 494 of our paper.   Reasons for believing that large temperature coefficients cannot be produced in this way will be found in section 5 of the same paper.

THE ACCELERATION OF THE ELECTRO-DEPOSI-TION OF HYDROGEN AND OXYGEN BY LIGHT OF SHORT WAVELENGTH.

By F. P. Bowden.

Received 17th March, 1931.

An investigation is being made of the mechanism of electro-deposition of hydrogen and oxygen from acid solutions. In the discharge of hydrogen for example, a hydrogen ion which is certainly hydrated moves up to the cathode and ultimately molecular hydrogen is evolved.

The nature of the electron transition which results in the discharge of the ion and the detailed mechanism by which the molecule is formed is by no means completely understood. If the hydrogen is to be evolved at a finite rate it is necessary for the potential to be considerably more negative than the reversible hydrogen electrode : this excess potential is called over-potential. This irreversibility is very dependent upon the chemical nature and physical state of the metal surface which acts as cathode. The kinetics of these processes have been worked[1] out and measurements made of the quantity of electricity which must be passed across the interface in order to establish the overpotential.[2] These measurements were consistent with the view that the pre-discharged hydrogen exists as dipoles oriented at the electrode surface : the interfacial potential is determined by the number and electric moment of these dipoles. With hydrogen it is the negative charge which is towards the electrode, with oxygen it is the positive charge, but from the similarity in the kinetics of these two reactions it is probable that the mechanism is very similar in each case. Energy of activation (with consequent increase in rate of discharge to form neutral molecules) could be supplied to the dipoles by raising the temperature or by increasing the interfacial potential. It seemed probable that the rate of discharge could also be accelerated by illuminating the electrode surface with light of suitable wavelength. On investigating this experimentally it was found that ultra-violet light caused a marked acceleration in each case : the shorter the wavelength the greater the acceleration.

The assumption of oriented dipoles at the surface can be little more than a convenient working hypothesis unless more knowledge of their detailed structure is available. Although it is easy to suggest ways in which the predischarged hydrogen dipoles can exist at the electrode it is difficult to decide the question with any certainty from the kinetics and the quantities involved. It seems probable that this light effect could give more definite information on this point. It should, for example, decide whether the electron transition, resulting in the ultimate formation of a neutral molecule, occurred between $\overset{-}{M} - \overset{+}{H}$ or between $\overset{-}{H} - \overset{+}{H}$. In the former case the magnitude of the light effect and the threshold frequency should be dependent on the nature of the metal forming the cathode : in

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[1] *Proc. Roy. Soc.*, A **126**, 107, 1929. [2] *Ibid.*, A **125**, 446, 1929.

the latter case it should be independent of the nature of the underlying metal.

A short account of some of the results already obtained is given here, but further experimental work is still in progress.

Experimental.

Hydrogen on Mercury Cathode.—The general arrangement of the cell and light source is shown in Fig. 1.

The platinum plate A acts as anode. B is the mercury cathode which can be illuminated by opening the shutter S. A 100 volt battery of small accumulators supplies the polarising current which flows between A and B : the magnitude of the current is controlled by variable resistances. The potential of the cathode is measured against a standard saturated calomel electrode C, an Einthoven string galvanometer being used so that no appreciable current is drawn from the electrode when its potential is being determined. Light from a mercury vapour lamp is condensed on to the surface of the electrode by large quartz condensing lenses. The complicated arrangement of the cell is to enable the electrolyte and the mercury cathode to be admitted without their coming into contact with the air. The electrolyte which is $N/5$ sulphuric acid is boiled out under reduced pressure and
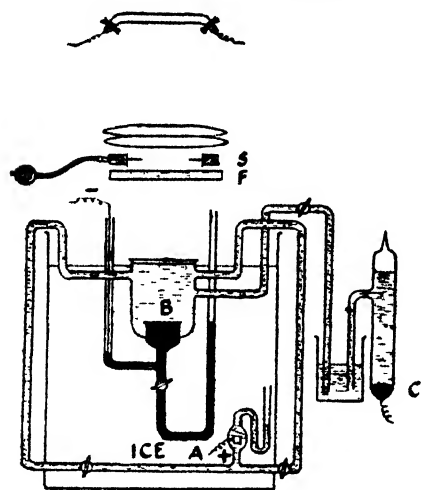
FIG. 1.

stored under hydrogen: it is then blown into the cell under hydrogen pressure. The mercury surface is allowed to grow under the electrolyte and is made cathodic during this process so that no Hg ions can enter the solution. These precautions are essential since minute traces of dissolved air, mercury ions or impurities have a very great effect on the electrode potential. Under these conditions, very small polarising currents cause a high overpotential which is steady and reproducible and varies in an orderly manner with the current density.[2] Polarising currents of 10^{-8} amps./cm.[2] cause an overpotential of about 0·5 volts. With these small currents it requires several hours of electrolysis before visible bubbles of hydrogen collect on the surface. The cell is maintained at constant temperature by a bath of melting ice.

On illuminating the electrode with ultra-violet light there is an immediate drop in the overpotential. The polarising current is then increased until the potential comes back to its original value. The necessary increase in current density is a measure of the increased rate at which hydrogen is being liberated at the cathode at that potential under the influence of light and may for convenience be called the photo-current. The photo-current can also be obtained directly from the magnitude of the fall of potential, since the relation between potential and current density is known. Using all the ultra-violet light from the mercury vapour lamp, photo-currents of about 5×10^{-6} amps./cm.[2] were obtained : this would

correspond to the discharge of about 5×10^{-11} gram ions of hydrogen per second by the action of the light. The potential of the cathode was -1.08 volts on the saturated calomel scale.

Determination of Threshold Frequency.—In Fig. 2 the logarithm of the photo-current is plotted against the wavelength of the incident light at a standard intensity.

The relation is approximately linear and the threshold is near 4000 Å.U. Light of longer wavelength has no appreciable effect.
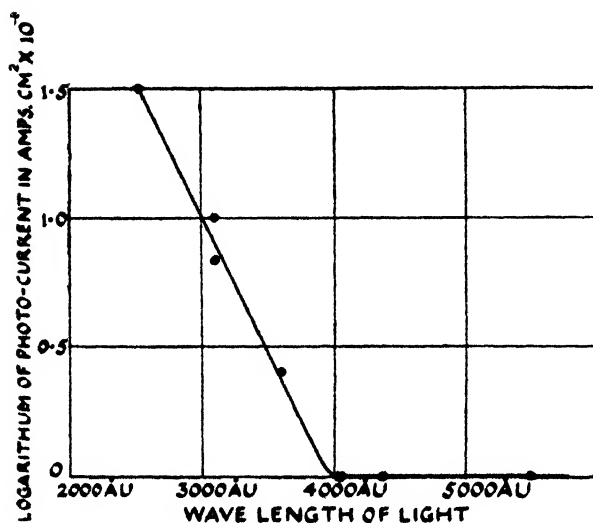
FIG. 2.
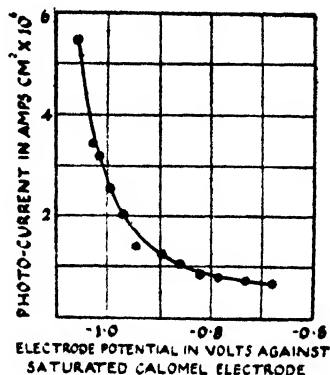
FIG. 3.

Relation between Photo-Current and Electrode Potential.—The magnitude of the photo-current for a constant light intensity is dependent upon the potential of the electrode. This is shown clearly in Fig. 3.

The photo-current decreases as the potential becomes less negative.

Oxygen on Platinum Anode.—The mercury was replaced by a square centimetre of bright platinum foil insulated underneath by a coating of glass. The experimental arrangements were as before except that the electrolyte was now saturated with oxygen and the platinum foil was made the anode. The oxygen overpotential on platinum is somewhat higher than that of hydrogen for the same current density.[1] On illuminating the anode surface keeping its potential constant, there is again a marked increase in the current flowing. The photo-current is of the same order as that observed for hydrogen; using all the ultra-violet light the photo-current was 2×10^{-8} amps./cm.^{2}, the electrode potential was $+1.34$ volts. The shorter the wavelength of the light the greater the photo-current but the threshold has not yet been determined with any accuracy.

The accuracy of this work was limited by the experimental difficulty of obtaining a range of intense monochromatic light in the ultra-violet. Light filters are troublesome and unsatisfactory in the far ultra-violet. A large quartz monochromator which will give intense monochromatic light down to 1800 Å.U. is, therefore, under construction. Further discussion of these results is deferred until the more precise measurements have been obtained.

Apart from its application to this particular field, the electrolytic method of studying the photo-chemistry of surface reactions has some advantages. The conditions at the surface can be controlled and surface reaction velocities of less than 10^{-13} gram ions per cm.^{2} per second can be followed merely by reading a micro-ammeter.

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THE PHOTOCHEMICAL DECOMPOSITION OF CHLORINE DIOXIDE IN CARBON TETRA-CHLORIDE SOLUTION.

By Y. NAGAI AND C. F. GOODEVE.

The photodecomposition of chlorine dioxide solutions in carbon tetrachloride was first studied by Bowen,[1] who found a quantum efficiency of unity, using blue and violet light and concentrations of ClO_2 between 0·0346 and 0·317 molar. Bodenstein and Schumacher,[2] in their discussion on the photochemical formation of Cl_2O_6, propose a mechanism for the decomposition of ClO_2, by which the quantum yield of unity could be explained. Bowen's method for measuring the absolute intensity of light, however, was not as accurate as more recent methods. The use of light containing wavelengths over almost the entire visible range of the spectrum may have caused further errors in these earlier determinations, and it became therefore of interest to repeat these measurements for chlorine dioxide solutions.

Experimental.

Chlorine dioxide was prepared by distillation at low pressures from a cooled mixture of H_2SO_4 and $KClO_3$ fractionated several times and dried with P_2O_5. It was dissolved in purified CCl_4 and placed for a short time in a blackened bottle in a thermostat. Considerable difficulty was experienced in transferring the solution to the reaction vessels. Suction applied to a pipette or exposure to air was found to cause considerable loss of the dioxide due to evaporation. This difficulty was obviated by sampling with pressure applied to the bottle and rapid removal to the reaction vessels.

During the preliminary experiments it was found that oxygen formed by the decomposition of ClO_2 carried away some of the latter compound with it, causing an error in the results. This was avoided by affixing a small double U-shaped tube to the top of the reaction cell. Solid KI and its solution placed at the lower bend retained all escaping Cl_2 and ClO_2, and was afterwards added to the bulk for titration.

The analyses were made by adding the solution to neutral KI solution

[1] E. J. Bowen, *J. Chem. Soc.*, **123**, 1199, 1923.
[2] M. Bodenstein and H. J. Schumacher, *Z. physik. Chem.*, **B5**, 233, 1929.

and determining the amount of liberated iodine. In neutral solutions chlorine dioxide reacts according to the equation

$$3ClO_2 + 5KI \rightarrow 2KIO_3 + 3KCl + 3I$$

and chlorine reacts in the normal way. A known quantity of acid is then added, when a further reaction takes place,

$$KIO_3 + 5KI + 6HCl \rightarrow 6KCl + 3H_2O + 6I$$
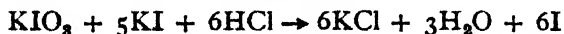
This second quantity of iodine is determined, from which the amount of ClO_2 is obtained. The quantity of acid used in the second reaction was also determined in most cases, and gave good agreement with the results obtained from the titration of iodine. In all experiments a balance was obtained, within the limits of experimental error, between the total amount of chlorine present initially and finally as Cl_2 and ClO_2. This is taken to indicate that no appreciable action of the reactants on the solvent nor loss by evaporation occurs.

Chlorine dioxide solution decomposes rapidly in the dark, and it was therefore necessary to measure the thermal reaction simultaneously with the photochemical reaction. Two samples were taken in the same way and placed in identical quartz cells of 3 cm. diameter and 1 cm. thickness. One cell was illuminated and the other placed in a black box, both in a thermostat. At the conclusion of an experiment the reactions were stopped by addition to KI solution. It has been assumed that the photochemical and thermal reactions proceed independently, and that the change due to light is given by the difference between the concentrations in the two cells.

The solution of ClO_2 in CCl_4 shows strong absorption below 4250 Å, even when as dilute as 4×10^{-3} mol/litre, but a rapidly decreasing absorption towards longer wavelengths.

A 1000 C.P. " Pointolite " (tungsten arc) lamp, operating from a battery supply, was used as the source of light. The curves of absorption coefficient wavelength for a large number of coloured liquids were determined by means of a Baly-tube and a standard absorbing screen, and from an examination of these curves a suitable combination of filters was readily determined. The light was first passed through a 30 mm. layer of a solution containing 5·5 per cent. of cobaltous sulphate ($7H_2O$) and 8 per cent. of ammonium thiocyanate, and then through a 30 mm. layer of a solution containing 25 per cent. of copper sulphate ($5H_2O$) and 0·04 per cent. of quinine sulphate. Spectroscopic examination confirmed the preliminary calculations in that the light that passed through outside of the range 4100 to 4200 Å was negligible. Both filters were immersed in the thermostat, but the heat developed in the first cell necessitated a water cooling coil.

The arrangement of the apparatus is shown in Fig. 1. The light from the point source is converged by the lens A, and passes through the window of the thermostat and filter cells B until it strikes the heavy brass shutter C. This shutter when closed presents a mirror to the oncoming light, thus preventing local heating. Immediately behind this is the aperture D, the diameter of which (20·8 mm.) is such that all light passing through it falls on the thermopile. The reaction cell E and the thermopile F follow in close contact. The thermopile used was of the Moll 80-element type, which was fitted with a quartz window and enclosed in a water jacket. A slight air pressure was maintained in the jacket to ensure against development of leaks. The thermostat was maintained at 20° C.

The *E.M.F.* produced in the thermopile was balanced by a micro-potentiometer circuit shown in Fig. 2, following that developed by Mr.

Guild,[4] of the National Physical Laboratory.   By this method the $E.M.F.$ necessary to give zero current (in a Moll galvanometer) is multiplied by the
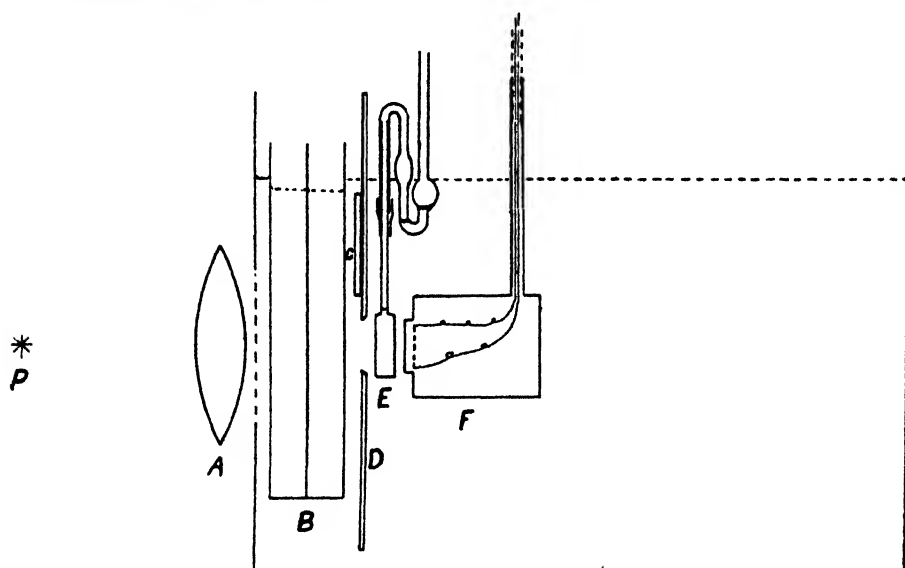
FIG. 1.

ratio R_3/R_1 (*e.g.* 10,000) and read on an ordinary standard milli-voltmeter. R_1 is a 0·1 ohm standard resistance, R_2 an iron wire resistance of about
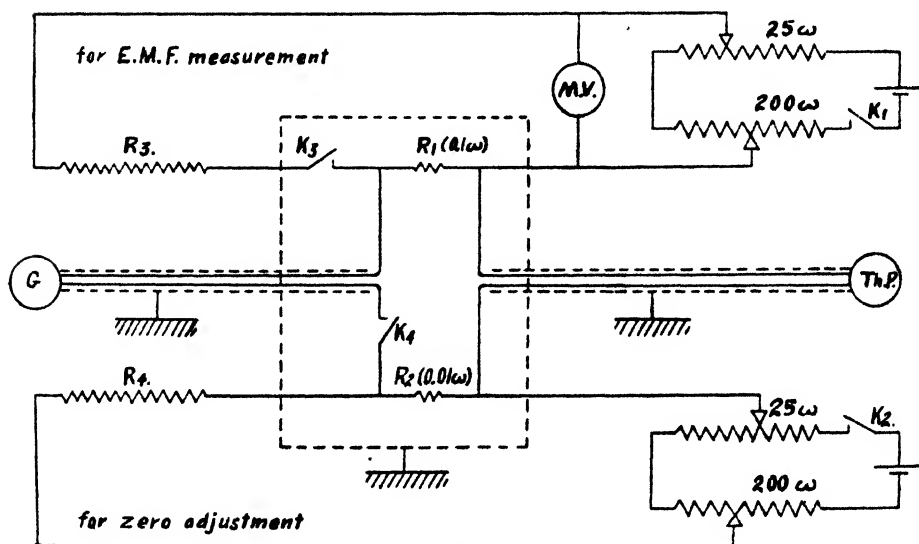
FIG. 2.

0·01 ohms, and R_3 and R_4 are ordinary plug-type resistances, 0-10,000 ohms.   Special switches K_3 and K_4 were constructed by drilling two holes close together in a large block of paraffin wax.   Contact was made by

[4] J. Guild, *J. Sci. Instr.*, **7**, 378, 1930.

lowering a weighted glass ⋂ into the holes, whereby mercury placed in them flooded a connecting groove. The mercury being at the same temperature in each hole, there was no contact potential when the circuit was closed. The switches and resistances were placed in a closed metal box which was earthed. It was found necessary to use earthed lead-covered cables to the thermopile and galvanometer. The galvanometer itself was placed on a vibration-proof block of concrete and enclosed in a draught-free cupboard.

In operation the lower circuit in the diagram was used to balance the residual $E.M.F.$'s from the thermopile so that the switch K_4 could be closed without producing a deflection of the galvanometer. The correcting potential may be applied in either direction by means of a reversing key K_2. The potential across the millivoltmeter was adjusted to about the value that was expected to be obtained (found by preliminary examination), and the switch K_4 and the shutter C operated simultaneously. A balance could be obtained and the millivoltmeter read within a few seconds. Measurements could be repeated with an accuracy of about 1 per cent.

The calibration of the thermopile, in absolute units, was carried out with a carbon filament lamp, supplied and standardised by the Bureau of Standards, Washington. This lamp has been restandardised by the National Physical Laboratory, and agreement within 1 per cent. obtained with the values given by the Bureau of Standards. The authors understand that either carbon or tungsten filament lamps can now be standardised for total radiation at the National Physical Laboratory. The thermopile was calibrated with its quartz window and with an internal air pressure the same as that used in the experiments. Calibration without the quartz window showed that 10 per cent. of the total radiation from the lamp is reflected or absorbed, and it is assumed that blue light is reflected to the same extent within the limits of error of the experiment.

The energy of the incident light was measured before and after each experiment with the cell E filled with pure CCl_4. With the concentration of ClO_2 used in these experiments, the incident light was completely absorbed.

Results.

Five experiments were carried out at 20° C. using the mean wavelength of 4150 Å. The results are indicated in Table I.

TABLE I.

Initial Conc. of ClO_2 (milli-mol./litres).	Time of Illumination (min.).	No. of Molecules Decomposed by Light × 10⁻¹⁸.	No. of Quanta Absorbed × 10⁻¹⁸.	Quantum Efficiency.
10·4	138·5	8·60	4·06	2·12
13·3	149	9·33	4·22	2·21
13·55	195	13·51	8·06	1·68
15·35	84	6·30	3·09	2·04
33·32	118	6·04	3·28	1·84

The average of these results is 1·98 ± 0·2, which is sufficient to indicate that two molecules are decomposed per quantum absorbed at the concentrations used. There was no indication of a change of this value with increasing concentrations and it probably holds over a much wider range. The value of unity found by Bowen can be attributed largely to his method

of measurement of the absolute intensity of the light used. It was found impossible to use higher concentrations of ClO_2 than the above owing to the increasingly rapid dark reaction. Bowen found a negligible dark reaction with concentrations as much as ten times that used here, but he used, apparently, a light intensity about fifty times as strong.

Discussion of Results.

In the wavelength region used in these experiments chlorine dioxide absorbs discontinuously, showing electronic-vibration-rotation bands.[5] The primary action of the light is therefore considered as electronic activation of the molecule. The energy of this activation may be used up either by re-emission of light (fluorescence) or by dissociation of the molecule on collision with a solvent molecule. In solution these collisions are many in the life of the activated molecule, and it is therefore probable that dissociation follows activation.

Chlorine dioxide may dissociate in three different ways :—

$$(1) \quad ClO_2 \rightarrow Cl + O_2$$
$$(2) \quad ClO_2 \rightarrow ClO + O$$
$$(3) \quad ClO_2 \rightarrow Cl + O + O.$$

The heat of decomposition of chlorine dioxide has recently been found by Janet I. Wallace to be about + 27 Cals.[6] Combining this with the heats of formation of oxygen and of chlorine atoms it can be shown that 119 Cals. are required for reaction (3), and with the heat of formation of chloric oxide[7] it can be shown that 80 to 85 Cals. are required for reaction (2). Both of these are much greater than the energy of 4150 Å. (69 Cals.). On the other hand, reaction (1) is endothermic to the extent of only 2 Cals. If this reaction can be assumed to take place, the quantum yield of (2) can be explained very simply by the following reactions :—

$$(4) \quad ClO_2 + h\nu \quad \rightarrow ClO_2{}^*$$
$$(5) \quad ClO_2{}^*(+ CCl_4) \rightarrow Cl + O_2(+ CCl_4) \quad . \quad (+ 67 \text{ Cals.})$$
$$(6) \quad Cl + ClO_2 \quad \rightarrow Cl_2 + O_2 \quad . \quad . \quad (+ 56 \text{ Cals.}).$$

It is to be noted that both these latter reactions are highly exothermic.

Collisions between activated and unactivated chlorine dioxide molecules are also possible, but it would appear improbable that the activated molecule would be able to withstand repeated collisions with the solvent molecules without decomposition. Furthermore, it has been found by Bodenstein, Harteck, and Padelt,[8] and confirmed by us, that gaseous chlorine dioxide is only slightly decomposed by light of this wavelength, the principal reaction being the photosynthesis of chlorine hexoxide. Collisions between two chlorine dioxide molecules must therefore result in association or in the formation of a higher oxide but not in decomposition.

This difference between the photoreaction in the gas and in solution favours the above mechanism in which the activated chlorine dioxide molecule is decomposed by collision with the solvent molecules. On the other hand, it has been found by Dickinson and Jeffreys[9] that chlorine dioxide is produced in large quantities in the photochemical decomposition of

[5] C. F. Goodeve and C. P. Stein, *Trans. Farad. Soc.*, **25**, 738, 1929.
[6] *Private communication.*
[7] C. F. Goodeve and Janet I. Wallace, *Trans. Farad. Soc.*, **26**, 254, 1930.
[8] M. Bodenstein, P. Harteck, and E. Padelt, *Z. anorg. Chem.*, **147**, 233, 1925.
[9] R. G. Dickinson and C. E. P. Jeffreys, *J.A.C.S.*, **52**, 4288, 1930.

chlorine monoxide in carbon tetrachloride solution, despite the fact that the absorption of light by chlorine dioxide is much greater than that due to the monoxide. It is highly probable that chlorine dioxide will decompose in the same way at 4358 Å., the wavelength used by Dickinson and Jeffreys, as at 4150 Å. An explanation of the formation of chlorine dioxide in the face of illumination which will quantitatively decompose it, may lie in the decomposition of chlorine monoxide by chlorine atoms, produced according to equation (5) with the subsequent regeneration of chlorine dioxide. Further work to identify the steps in this reaction is being carried out in these laboratories.

The possibility of short chain reactions occurring in the photodecomposition of chlorine dioxide is still to be considered. The excess energy of reactions (5) and (6) will be dissipated immediately to the solvent thus preventing further action of the chlorine and oxygen molecules. A reaction producing chloric oxide or chlorine monoxide in place of reaction (6) would be highly endothermic and is therefore improbable. There appear to be no other possibilities from which chains can arise. On the other hand chlorine atoms produced in (5) cannot be used up in any other way than according to (6) except by recombination of two chlorine atoms. The collision probability of this recombination is very small, unless the collision efficiency of reaction (6) is low, producing a high concentration of chlorine atoms. At all events the probability of reaction (6) taking place is much greater than that of recombination of chlorine atoms. It is therefore to be expected that the quantum efficiency of this photodecomposition should be two molecules per quantum absorbed, as has been found above.

The authors wish to thank Professor F. G. Donnan for his interest in this research, and one of the authors (Y. N.) to the Ramsay Memorial Fellowship Trust for a fellowship awarded to him.

Summary.

The experimental technique for the measurement of the quantum efficiency of a photochemical reaction in solution is described, including a simple but accurate method for measuring thermopile $E.M.F.$'s. The quantum efficiency of the photodecomposition of chlorine dioxide has been found to be $2 \cdot 0 \pm 0 \cdot 2$ molecules per quantum for violet light and over a range of concentrations. The following mechanism has been suggested and supported by thermal and spectroscopic data : —

$$\begin{aligned}
(1) \quad & ClO_2 + h\nu && \rightarrow ClO_2^* \\
(2) \quad & ClO_2^*(+ CCl_4) && \rightarrow Cl + O_2(+ CCl_4) \\
(3) \quad & Cl + ClO_2 && \rightarrow Cl_2 + O_2
\end{aligned}$$
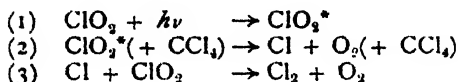
The possibility of chains has been discussed, and they are shown to be improbable.

The Sir William Ramsay Laboratories of
Physical and Inorganic Chemistry.

GENERAL DISCUSSION.

On Part III., Paper 4.

Mr. E. J. Bowen (*Oxford*) (*communicated*) : I am entirely in agreement with the remarks of Goodeve and Nagai on the question of the accuracy of my earlier work on the decomposition of carbon tetrachloride solutions of

ν	$\lambda [\text{Å}]$	Cal/Mol	Volts
10000	10000	30	
	9000		
	8000		
	7000	40	
	6000	50	2.0
20000	5000	60	
	4000	70	3.0
		80	
30000		90	4.0
	3000	100	
		110	
40000		120	5.0
		130	
50000	2000	140	6.0
		160	7.0
60000		180	8.0
70000		200	9.0
80000		220	10.0
		240	
90000		260	11.0
100000	1000	280	12.0
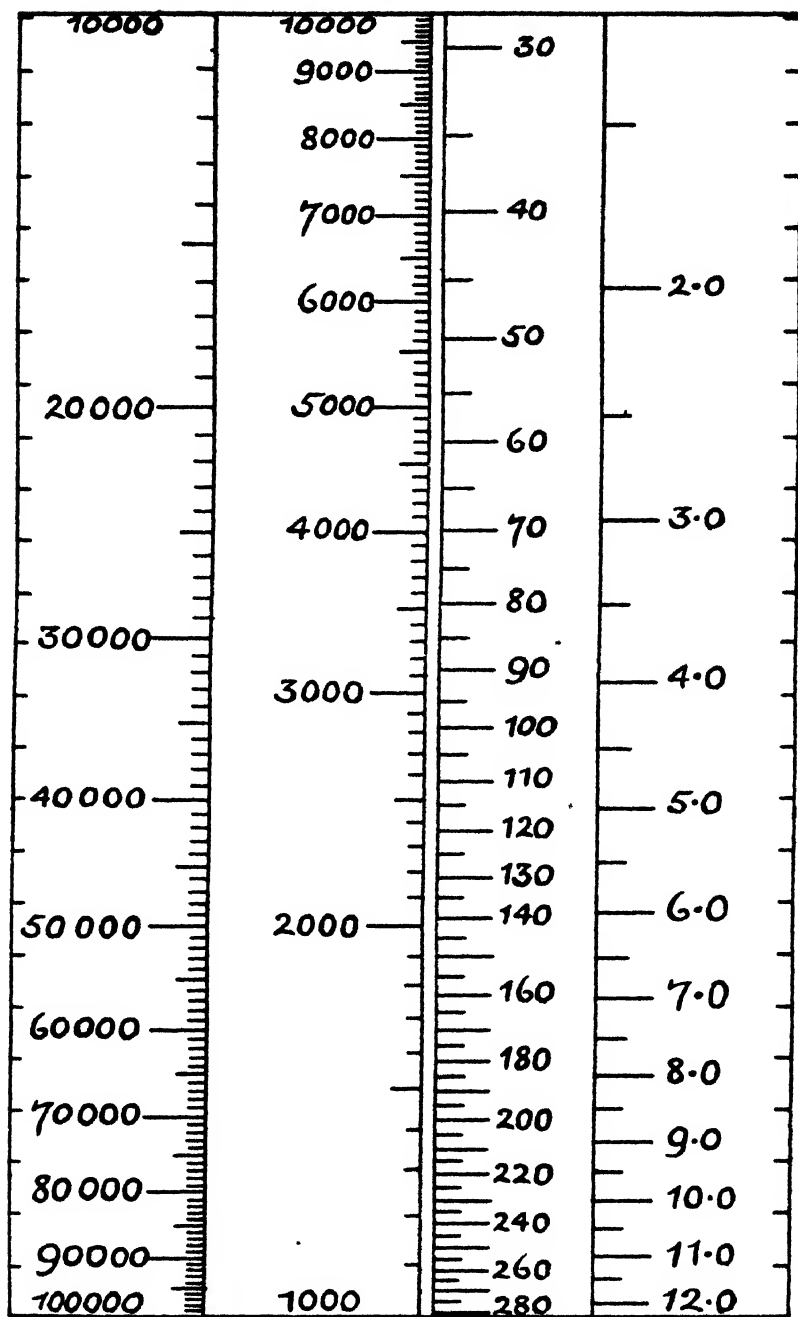
chlorine dioxide. The experiments were carried out with very crude apparatus. Some experiments have recently been made by Mr. Cheung and myself to discover whether chlorine hexoxide, which is formed in the gaseous photo-decomposition, is also formed in the photo-decomposition in carbon tetrachloride solution. The reaction was followed by titration with ferrous sulphate and with titanous sulphate. As chlorine hexoxide produces chlorate ion with water, which is reduced by the latter but not by the former in the cold, its formation would be shown by an increasing difference in the titrations during the decomposition. No indication of the formation of chlorine hexoxide was found.

Miss Janet I. Wallace (*London*), said: With reference to the paper of Nagai and Goodeve, the heat of dissociation of chlorine dioxide is still in doubt. It was determined by Booth and Bowen[1] as 23·5 Cals., and by Mayer[2] as about 25 Cals. A redetermination is being carried out and preliminary measurements gave a fairly consistent value in the neighbourhood of 34 Cals. Subsequent measurements, however, have indicated that the value is nearer to 27 Cals. Definite results will be published in the near future.

Professor R. Mecke (*Heidelberg*) said: I would like to present to the meeting a diagram which has been kindly designed at my request by Mr. W. H. J. Childs while he was staying with me at Bonn. It has proved to be very helpful in turning energy amounts into the four different energy units now commonly used in photochemical work : (i) wavelength in Å.U. ; (ii) frequencies in wave-numbers cm.$^{-1}$; (iii) heats of reaction in cal./mol. ; (iv) electronic impact energy in volts.

The range covered in this diagram is the ordinary range of spectroscopic work, λ10,000 – λ1000 Å.U., but by multiplying or dividing the numbers by factors of ten it might easily be extended to any limit wanted. I think the table needs no further explanation. I will only state that I have used it many times, and I have found it very convenient in the rapid determination of the spectroscopical energy equivalence while discussing the different primary processes of photochemical reactions.

[1] *J. Chem. Soc.*, 342, 1925.
[2] *Diss.*, Hannover, 1924 (unpublished).

THE PHOTOCHEMICAL REACTION BETWEEN IODINE AND POTASSIUM OXALATE IN AQUEOUS SOLUTION.

BY PROFESSOR A. J. ALLMAND AND K. W. YOUNG.

The well-known work of Berthoud and Bellenot[1] on this reaction left certain points concerned with the effect of frequency undecided. The experiments described below were designed to fill this gap. Assuming the correctness of the work of the above authors on the kinetics of the reaction, as also their general views on its mechanism, supported as the latter are by the experiments of Briers, Chapman and Walters,[2] we used throughout a

[1] *Helv. Chim. Acta,* 7, 307, 1924 ; *J. Chim. Physique,* 21, 308, 1924.
[2] *J. Chem. Soc.*, 562, 1926.

reaction mixture of constant composition and studied the effects of (*a*) true variation of intensity, (*b*) variation of wavelength, and (*c*) variation of temperature, working chiefly with the series of monochromatic rays afforded by the quartz-mercury lamp used in conjunction with suitable filters.

Experimental Methods.

The temperature coefficient of this reaction has been shown by Berthoud and Bellenot to be high, *viz.* 3·22 for red and 3·15 for blue light in the temperature region 25°-40°. A close temperature control was thus indicated. In addition, the Moll surface thermopiles normally employed in this laboratory register appreciable "zero" readings when used in air, readings moreover which fluctuate in consequence of unavoidable air currents. A thermostat was therefore designed to hold both reaction cell and thermopile, and has proved very successful in practice, true zero readings and exactly reproducible thermal *E.M.F.*'s being obtained. It is of copper, 40 × 30 × 25 cm. In the centre of either end is a circular aperture, ·8 cm. in diameter, which can be closed by a crystal quartz or a glass window, held in a copper seating by rubber washers and wing-nuts. It is provided with a copper cover, screwed down on to a flange and drilled with holes through which pass the upper ends of the heating lamps, thermo-regulator and stirrer. A rectangular opening allows of the insertion of the holder of the reaction cell, a U-shaped brass trough which is soldered on to and immediately behind a circular aperture of 2·2 cm. diameter in a blackened metal screen, the whole depending from two brass rods which, in their turn, are supported by a flat metal panel which rests flush on the top of the thermostat cover. By means of adjustment by screws, the position of this holder behind the thermostat window can be very exactly reproduced. The thermopile casing depends from a similar metal lid, which slides between metal guides over a suitable aperture in the thermostat cover, being attached to the lid by a circular clamp which allows of either a vertical or a pendulum-like motion.

The casing itself consists of a flanged brass tube (11 cm. long; 8 cm. diameter), of which the front end is provided with a quartz window 4 cm. in diameter and the rear end closed by a brass screw cap, both made water-tight by rubber washers. The thermopile [3] is rigidly supported inside the casing so that its face occupies a definite position behind and parallel to the quartz window, the leads being brought out through a brazed-on side-tube held by the circular clamp. A blackened metal shutter is placed between the back of the reaction cell and the front of the thermopile casing.

The cells employed were of quartz or of glass with plane-parallel circular ends, 4·5 cm. deep internally, of diameter 2·5 to 3 cm. and of volume 25 to 30 c.c., and were provided with stoppered side-tubes made sufficiently long to project above the outer level of the thermostat water. Distilled water was used for this last purpose and with satisfactory results—the Tyndall cone produced by the entering beam was very feeble.

The 110-volt lamp was of vacuum type. The applied voltage was kept constant by means of a Tirrill regulator. A suitably convergent beam was obtained by means of 10 cm. quartz condensers in conjunction with diaphragms. The Moll thermopile was of 1 cm. diameter, the thermal *E.M.F.*'s being measured to the nearest microvolt by means of a micro-

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[3] With its outer cone removed and its inner cone treated as described elsewhere—see *J. Chem. Soc.*, 2701, 1930.

potentiometer and galvanometer. Its sensitivity after the treatment referred to was $9 \cdot 9 \times 10^{-6}$ volt per H.K. at one metre. This sensitivity was found to vary somewhat with the thermostat temperature, first rising and then falling off as the latter was raised. Three measurements of this variation showed the same qualitative behaviour, and two of them agreed closely quantitatively. The temperature of maximum sensitivity fell in every case between $27°$-$30°$. The measurements in the present paper were made at $30°$ and $35°$, and the correction for the lower sensitivity at the higher temperature is only $0 \cdot 3$ per cent.

The filters used were as follows :—

579 $\mu\mu$.

Corning Glass Filter G. 34 R, $1 \cdot 98$ mm. thick. Transmits 35 per cent. of 579 $\mu\mu$ and $<$ 1 per cent. of 546 $\mu\mu$. Also a little red and infra-red.

546 $\mu\mu$.

(a) Schott Glass Filter F. 4313, 3 mm. thick. Transmits $90 \cdot 3$ per cent. of 579 $\mu\mu$, $89 \cdot 5$ per cent. of 546 $\mu\mu$ and $<$ 1 per cent. of 436 $\mu\mu$.

(b) Corning Glass Filter G. 555 BE, $4 \cdot 33$ mm. thick. Transmits $81 \cdot 8$ per cent. of 546 $\mu\mu$ and 52 per cent. of 436 $\mu\mu$.

The combination passes small quantities of red and infra-red.

436 $\mu\mu$.

(a) 5 mm. layer of $0 \cdot 09$ per cent. Victoria Blue solution.

(b) 5 mm. layer of 4 per cent. quinine sulphate solution.

The whole made up with three glass plates into a composite cell. Transmits 55 per cent. of 436 $\mu\mu$.

405 $\mu\mu$.

(a) 5 mm. layer of $0 \cdot 0121$ per cent. Diamant Fuchsin solution.

(b) 5 mm. layer of $0 \cdot 02$ per cent. quinine bisulphate solution.

The whole made up into a composite cell by means of three glass plates. Transmits 23 per cent. of 405 $\mu\mu$.

365 $\mu\mu$.

Corning Glass Filter G. 586 AW, 5 mm. thick. Transmits 18 per cent. of 365 $\mu\mu$.

The variation of intensity was effected by inserting in the path of the beam a greater or smaller number of thin parallel glass plates, separated by air-gaps from one another, each plate weakening the intensity by about 10 per cent. owing to reflection loss.

The $K_2C_2O_4$ and KI used were recrystallised, and the iodine resublimed. The solutions used throughout had the following initial composition : $[I_2]$ $0 \cdot 00257$ $M.$; $[KI]$ $0 \cdot 01018$ $M.$; $[K_2C_2O_4]$ $0 \cdot 76$ $M.$

In the main experiments, the plan adopted was to carry out a complete series of measurements with one·fixed wavelength before passing to another, a set of readings at varying incident intensities being made first at one standard temperature ($30°$ C.) and then at another ($35°$ C.). In each separate experiment, the procedure was to fill the cell with distilled water, place it in the thermostat and measure the transmitted intensity. The cell was then emptied out, filled up to a calibration mark on the side tube with the reacting solution and placed in position in the thermostat : when it had reached the reaction temperature, insolation was commenced and the transmitted intensity again measured, the difference representing the energy absorbed by the photolyte. This measurement was repeated at the end of the run, as also was the measurement of the transmission of

the water-filled cell, this last reading affording a check on the constancy of the intensity. The mean value of the absorbed energies at the commencement and at the end of a run was taken for the purpose of quantum efficiency calculations.

The reaction was followed by titration of the contents of the cell at the end of the experiment with $Na_2S_2O_3$, the times of insolation being so arranged that the amounts decomposed were always of the same order—about 16 per cent. of the total available iodine. Determinations of the dark reaction rates were carried out, and the figures found subtracted from the observed rates in light. This thermal correction amounted to 5-30 per cent. of the total reaction, the figure of course depending on the light intensity used, as also to a lesser degree on the temperature. The temperature coefficient of the dark reaction was 6·45, corresponding to an activation energy of 34,400 cals. Berthoud and Bellenot found 4·86 in the region of 70° C., giving E = 37,400 cals.

It may be added that a number of preliminary experiments were done using 1000-2000 c.p. water-cooled metal filament lamps, in conjunction with one or other of a series of Corning Glass Filters transmitting bands of light in one part or another of the visible spectrum. They served to indicate the order of the reaction rates to be measured, and also plainly showed γ to be an inverse function of the intensity. The values of the latter were high in these experiments, and γ never exceeded o·6. An experiment of this kind was also done using a Corning Glass filter G 554 FF, 3·5 mm. in thickness, which transmits infra-red radiation, but which is opaque in the visible. The decomposition measured was far greater than could be accounted for by the slight rise in temperature (o·2°) caused by the high infra-red intensity.

Results.

Effect of Intensity.—Table I. contains the actual data obtained with the 579 $\mu\mu$ line, the incident intensities being expressed by thermopile readings in micro-volts and the velocity as micro-mols. of iodine reacted per hour. Fig. 1 shows graphically the results given by the four mercury lines worked with, plotted in the form of velocity against $I_0^{o \cdot 5}$. The direct proportionality is evident, and is in agreement with the data of Berthoud and Bellenot, obtained with intermittent light.

TABLE I.

(a) 30° C.			(b) 35° C.		
I_0.	$I_0^{o \cdot 5}$.	Velocity.	I_0.	$I_0^{o \cdot 5}$.	Velocity.
64·01	8·00	9·38	81·0	9·0	17·95
53·05	7·28	.8·59	66·6	8·16	16·52
37·09	6·09	7·07	54·76	7·4	14·95
			46·02	6·78	13·22
			43·32	6·58	12·59
			33·87	5·82	10·86
			19·45	4·42	8·40

In the case of the 405 $\mu\mu$ line, the maximum intensity available was so small as to preclude the possibility of accurate work at lower intensities. The same was true of the band in the region of 675 $\mu\mu$, isolated by means of a Schott glass filter F. 4512 2 mm. thick, from the spectrum of the metal

filament lamp. In both cases, several measurements were made at approximately the same intensity at each temperature. For the purpose of calculating γ and T.C., the mean values of the respective figures were used and, in addition, the $I_0{}^{\sigma\cdot 5}$ rule assumed when necessary.

Effect of Temperature.—From the curves in Fig. 1, together with the data for 405 $\mu\mu$ and 675 $\mu\mu$ just mentioned, the temperature coefficients for the reaction in the different monochromatic beams can be calculated. These values, referred to a rise in temperature of 10° C., are given in Table II. It will be noted (i) that they are high, (ii) that there is fair agreement with the figures obtained by Berthoud and Bellenot (3·22 and 3·15 in red and blue light respectively), and (iii) that the temperature coefficient appears to pass through a minimum in the yellow, and certainly rises rapidly for the shorter wavelengths. It is interesting that the only other recorded case of an inverse relation between T.C. and λ is furnished by the iodine-sensitised oxidation of aqueous hydriodic acid.[4]

A suggested explanation of the very curious course of the figures in Table II., together with a description of further relevant experiments, are given elsewhere.[5] It is shown to be quite probable that the true T.C. over

FIG. 1.

the whole frequency range covered is constant at about 3·0 ± 0·2. On the other hand, it also seems plausible to conclude from the data referred to
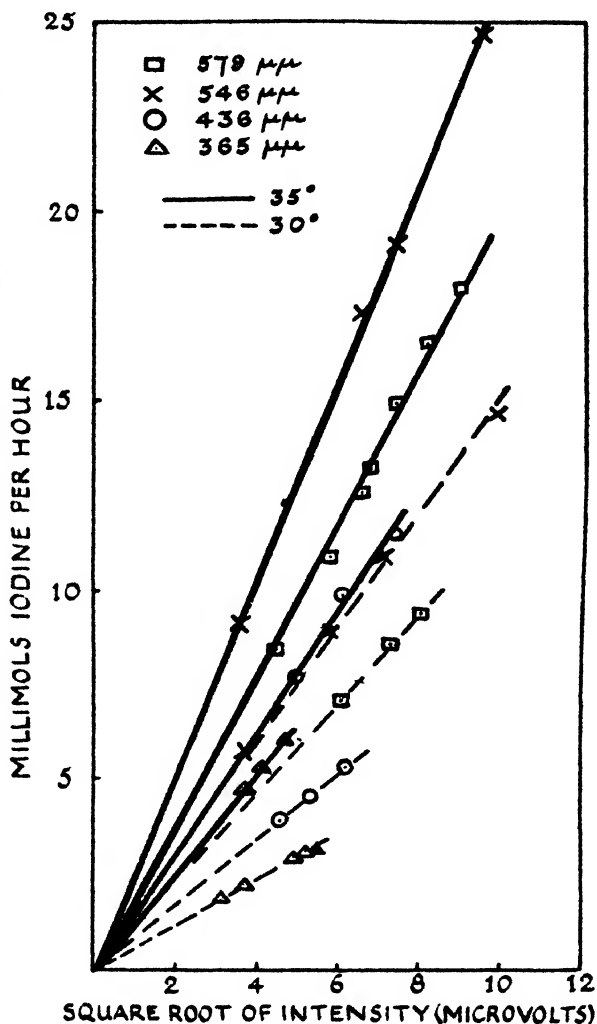
TABLE II.

Wavelength ($\mu\mu$) . . .	365	405	436	546	579	675
Temperature coefficient .	4·88	3·55	3·40	3·06	2·78	3·40

[4] Padoa and Vita, *Gazzetta*, **55**, 87, 1925.
[5] See Style and Young, this volume, p. 493.

that the T.C. might increase with increasing wavelength as is frequently found in other cases.

Effect of Wavelength on Quantum Efficiency.—In reactions of the $I^{0.5}$ type, γ is a function both of intensity and of concentration, and moreover will also depend on the extinction coefficient of the light used, quite apart from any effect of frequency on the efficiency of the primary process resulting from absorption. Attempts to estimate this latter effect by a mere comparison of quantum efficiencies must therefore give misleading results. In Fig. 2 are plotted the values of γ found in our experiments at 30° and at 35° for two different conditions of insolation, *viz.*, for an incident intensity (full squares and circles), and for an absorbed intensity, of 36×10^{-6} volt,
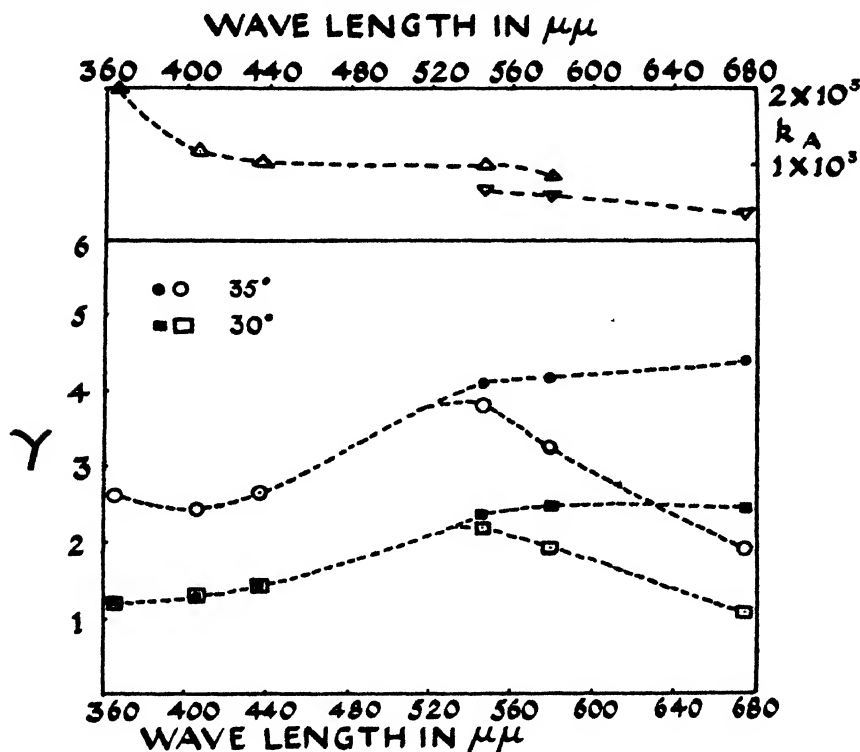
FIG. 2.

independent of wavelength. Where absorption was complete, as with the 365 $\mu\mu$, 405 $\mu\mu$, and 436 $\mu\mu$ lines, the two curves of course coincide. In such cases the values of γ were derived from the data in Fig. 1 ; in other cases they were calculated from the measured absorptions of the solution. Whilst the values of γ compared at equal incident intensity increase with increasing λ, the values at equal absorbed intensity are seen to pass through a marked maximum in the green (the minimum shown in the 35° C. curve in the violet is connected with the anomalous temperature coefficients mentioned in the last section).

It has been suggested [6] that, for such $I^{0.5}$ reactions, the constant k_A of the expression,

$$\text{velocity} = k_A \times (\text{rate of quantum absorption})^{\frac{1}{2}},$$

[6] Allmand, *J. Chem. Soc.*, 1557, 1929.

a constant quite analogous to Γ, the *coefficient of utilisation* of Tian[7] as applied to $I^{1.0}$ reactions, could usefully be taken as a measure of the relative efficiency of different wavelengths. In the case of the photodecomposition[8] of H_2O_2, where γ was observed to fall off with increasing v, this treatment of the experimental data led to values of k_A which increased with increasing frequency, as often occurs with $I^{1.0}$ reactions.

One of the expressions deduced on this basis is the following—

$$\gamma = \frac{2k_A}{I_0^{\frac{1}{2}} . c^{\frac{1}{2}} . a^{\frac{1}{2}} . (1 + 10^{-\frac{1}{2}acl})}$$

where a is defined by $I_0/I = 10^{acl}$, c is in mols./litre, l in cm., and I_0 in quanta/second. Then, for a whole series of wavelengths, with the same incident intensity in ergs./cm²/second, the same photolyte, the same depth of cell and the same cross-section of beam, we shall have

$$k_A \propto \gamma . a^{\frac{1}{2}} . \lambda^{\frac{1}{2}} . (1 + 10^{-\frac{1}{2}acl}).$$

In the present case, we have no exact values of a covering the whole range of wavelengths for the particular reaction mixture used, nor do we know definitely whether all the absorbed quanta can effect primary activation, or whether there is an appreciable internal light filter effect.

Brode[9] has carried out measurements on a single very dilute solution of I_2 in KI ([I_2] 0·00015 M; [KI] 0·00075 M) and from his graph, very approximate figures for a may be deduced. These are

$\lambda(\mu\mu)$	365	405	436	546	579
$a \times 10^{-3}$	7·7	2·1	1·2	0·32	0·17

Winther[10] has measured the extinctions, between 265-450 $\mu\mu$, of dilute solutions of aqueous iodine made 1 N with respect both to KI and to HCl. His figures for the most concentrated of these solutions ([I_2] 0·00797 M) are as follows :—

$\lambda(\mu\mu)$	365	405	436
$a \times 10^{-3}$	10	2·8	1·3

and agree reasonably well with those of Brode.

Lastly, from the determinations of incident and transmitted energy made in the course of this work, using the mixture [I_2] 0·00257 M + [KI] 0·01018 M + $K_2C_2O_4$, the following rough figures may be calculated :—

$\lambda(\mu\mu)$	546	579	675
a	76	34	7·3

These are probably too low for both the 546 $\mu\mu$ and the 579 $\mu\mu$ lines, in consequence of the presence of infra-red radiation not removed by the filters used, and only slightly absorbed by the photolyte. Nevertheless, the extent of disagreement with Brode's figures is surprising, and suggested that the a values for the I_2 molecule and the I_3' ion were widely different, corresponding to the fact that calculations based on existing data on the value of $K = [I_3']/[I_2][I']$ showed the ratio [I_2]/[I_3'] to be about 2 : 1 in Brode's solution and about 1 : 5 in ours.

This conclusion, of course, is not in accord with the agreement between the results of Brode and of Winther, and measurements carried out with the

[7] *Ann. Physique*, 5, 248, 1916.
[8] Allmand and Style, *J. Chem. Soc.*, 619, 1930.
[9] *J. Amer. Chem. Soc.*, 48, 1877, 1926.
[10] *Z. physikal. Chem.*, 108, 236, 1924.

546 $\mu\mu$ line did not support it. A saturated aqueous solution of iodine at 25° (0·00133 M) did not change in transmission when an equimolecular amount of solid KI was added, and even a 30-fold excess of the latter only resulted in an increase in the transmission of the cell in use from 72·4 to 76·0 per cent. (measurements with filtered light, 2-cm. Moll thermopile and potentiometer). The value of a obtained in this case (131) was confirmed by measurements, using spectrally dispersed light (monochromator-linear thermopile-Paschen galvanometer). A solution of composition [I_2] 0·00478 M + [KI] 0·010 M gave $a = 134$. Diluted with an equal volume of water, a became 130. This coincidence between the extinction of I_2 and of I_3' is of interest for several reasons, and is being further investigated.

The data available at the moment will obviously not allow of an accurate evaluation of the effect of λ on k_A. But it is probable that they will suffice to give a true qualitative picture. Consequently, using the formula,

$$k_{A'} = \gamma . a^{\frac{1}{2}} . \lambda^{\frac{1}{2}} . (1 + 10^{-\frac{1}{2}ael}),$$

k_A' values have been calculated from the results of the experiments done at 30° and at a constant incident intensity of 36×10^{-6} volt, using both Brode's a values (i) and also our own rough data given above (ii). The results are as follows:—

$\lambda(\mu\mu)$ . .	365	405	436	546	579	675
(i) $k_{A'} \times 10^{-3}$.	1·98	1·18	1·03	0·99	0·85	—
(ii) $k_{A'} \times 10^{-3}$.	—	—	—	0·65	0·57	0·33

The figures are plotted in Fig. 2. They show at all events no sign of any maximum in the green, and whether the inflexion in this region is of significance cannot be stated at present. Their increase with increasing frequency suggests that the tendency for the temperature coefficient to increase somewhat with increasing wavelength represents a real effect. The sudden rise at 365 $\mu\mu$ is most probably due to diffusion of the "catalyst" from the absorbing layer into the bulk of the solution—the derivation of k_A assumes such diffusion not to take place.

The Mechanism of the Photochemical Reactions of Aqueous Iodine.

The mechanism originally suggested by Berthoud and Bellenot for the $I_2 - K_2C_2O_4$ reactions explains satisfactorily the great majority of experimental facts, although the assumption that the reaction $2I + I' \rightarrow I_3'$ proceeds more rapidly than $2I \rightarrow I_2$ is open to objection,[11] and in addition, if effective light absorption is due solely to I_2, and not to I_3' molecules, the average length of the observed chain is at first sight difficult to reconcile with the high temperature coefficient, assuming this to correspond to a true activation energy of perhaps 21000 calories. To explain their results on the reaction between I_2 and KNO_2, Berthoud and Berger[12] assume the same primary mechanism, followed by the intervention of HIO. Whilst they are successful in deducing a velocity expression in accord with the particular facts, it has been pointed out[13] that the tacit assumption is made that $2I + H_2O \rightarrow HIO + H^. + I'$ proceeds more rapidly than $2I + I' \rightarrow I_3'$, whereas the opposite is assumed in the case of the $I_2 - K_2C_2O_4$ reaction. Finally, the work of Rideal and Williams[14] and of Kistiakowsky[15] has

[11] Griffith and McKeown, *Photo-processes, etc.*, p. 452, 1929.
[12] *Helv. Chim. Acta*, 11, 354, 1928.
[13] Griffith and McKeown, *ibid.*, p. 491.
[14] *J. Chem. Soc.*, 127, 258, 1925.
[15] *J. Amer. Chem. Soc.*, 49, 976, 1927.

shown γ to be two in the case of the reaction $I_2 + 2Fe^{\cdot\cdot} \rightarrow 2I' + 2Fe^{\cdot\cdot\cdot}$, independently of λ and of c, and possibly also of T. Every reasonable explanation of this result must start from the assumption that the I_3' ion is activated by light.

It is clearly desirable to formulate a view of the primary light action and of those processes immediately succeeding it which will account for all the above reactions equally well. This proves to be difficult, as long as effective activation by light is regarded as confined either to I_2 molecules *or* to I_3' ions. The suggestions which follow derive in part from the mechanism recently proposed by Dickinson and Ravitz [16] for the C_2O_4'' and $Fe^{\cdot\cdot}$ reactions, as also for the $FeCy_6'''$ reduction worked on by them, and in part from our observation that, at 546 $\mu\mu$, the extinction coefficients of I_2 and I_3' are practically identical.

We suggest the following series of processes to be taking place in an insolated solution containing I_2 and I' ions :—

$$I_3' + h\upsilon \rightarrow 2I + I' \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1a)$$
$$I_2 + h\upsilon \rightarrow 2I \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1b)$$
$$I' + I_2 \rightleftharpoons I_3' \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$
$$I' + I \rightleftharpoons I_2' \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$
$$I + H_2O \rightarrow OH + H^{\cdot} + I' \qquad . \qquad . \qquad . \qquad (4)$$
$$OH + I' \rightarrow OH' + I \qquad . \qquad . \qquad . \qquad . \qquad (5)$$
$$2I_2' \rightarrow I_3' + I' \qquad . \qquad . \qquad . \qquad . \qquad (6a)$$
$$2I \rightarrow I_2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (6b)$$
$$I_2' + I \rightarrow I_3' \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (6c)$$
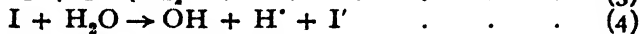
As first approximations (i) the efficiency of reactions 1a and 1b and (ii) the extinction coefficients of I_3' and I_2 are supposed to be the same for any given wavelength of light.[17] This being the case, it follows that the rate of primary formation of I atoms will only depend on the total concentration of titratable iodine, *i.e.* on $[\Sigma I_2] = [I_2] + [I_3']$, and not on $[I']$, *i.e.* on the ratio $[I_2]/[I_3']$. The formation of I_2' ions (process 3) was first proposed by Wagner [18] to account for certain phenomena in the thermal reactions between I' ions and $Fe^{\cdot\cdot\cdot}$ or $FeCy_6'''$ ions, and was applied to the corresponding photochemical reactions by Dickinson and Ravitz. The equilibria $K_2 = [I_3']/[I_2][I']$ and $K_3 = [I_2']/[I][I']$ are both assumed to be approached from either side with such rapidity as to persist during intense insolation of the solution, either in absence or in presence of an added acceptor for the I atoms. In addition, the ratio $K_3[I'] = [I_2']/[I]$ is assumed to be high.

The plausibility of process 4 is difficult to estimate with any degree of exactness. We can, for example, put

$$H_2O \text{ (liquid)} \rightarrow H \text{ (gas)} + OH \text{ (gas)} - 120 \text{ Cals.}$$
$$H \text{ (gas)} + I \text{ (gas)} \rightarrow HI \text{ (gas)} + 69 \text{ Cals.}$$
$$HI \text{ (gas)} \rightarrow H^{\cdot} \text{ (aq.)} + I' \text{ (aq.)} + 20 \text{ Cals.}$$

whence

$$I \text{ (gas)} + H_2O \text{ (liquid)} \rightarrow OH \text{ (gas)} + H^{\cdot} \text{ (aq.)} + I' \text{ (aq.)} - 31 \text{ Cals.}$$
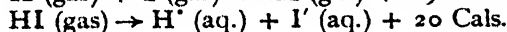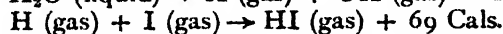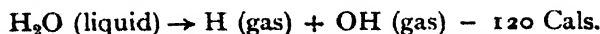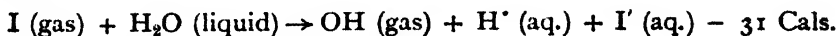
and it is probable that, for the reaction

$$I \text{ (aq.)} + H_2O \text{ (liquid)} \rightarrow OH \text{ (aq.)} + H^{\cdot} \text{ (aq.)} + I' \text{ (aq.)}$$
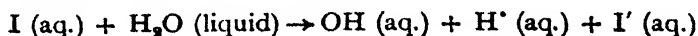
[16] *J. Amer. Chem. Soc.*, **52**, 4770, 1930.
[17] The second assumption will certainly not be true in the middle and shorter ultra-violet.
[18] *Z. physikal. Chem.*, **113**, 261, 1924.

the heat effect is of the same order. The uncertainty involved in such a figure is very considerable, but, on the assumption that no further energy of activation is required, and taking into account (i) the very high, but essentially unknown, collision number involved (if indeed one may speak of a collision number in this connection), and (ii) the contribution furnished by the surplus energy of the originally absorbed quantum, which varies from $2·5$ Cals./atom of iodine at $700\ \mu\mu$ to about $22·5$ Cals. at $350\ \mu\mu$, and which may certainly be available under the conditions of experiment, it seems quite possible that (4) may occur sufficiently rapidly to account for the experimental results in the $I_2 - KNO_2$ reaction, which, as will be seen, is the reason for its introduction. Process 5 is strongly exothermic, and will take place easily. It will be noticed that the sequence of (4) and (5), of course accompanied by $H^{\cdot} + OH' \to H_2O$, does not lead to disappearance of I atoms or to change in the composition of the solution. Whichever of the reactions 6 actually takes place, or whether more than one of them have velocities of the same order, are immaterial points ; in view of the nature of (2) and (3), the different reactions 6 are equivalent to one another. It is, however, assumed that the rate of (6) is low compared with that of any other reaction whatever shown as disposing of either I atoms or I_2' ions.

On the basis of the above assumptions, there will be in such an insolated solution a stationary value of [I] given by

$$[I] = \frac{k_1 I_0 [\Sigma I_2]}{k_3 [I']} = \frac{[I_2']}{K_3 [I']}.$$

Here, as later, it is assumed that the absorption of the active light is slight.

In the presence of acceptors, we shall have the following :—

Ferrous Ions and Ferricyanide Ions.—Here the mechanism is simply that of Dickinson and Ravitz, *i.e.* $Fe^{\cdot\cdot} + I_2'' \to Fe^{\cdot\cdot\cdot} + 2I'$ and $FeCy_6''' + I_2' \to FeCy_6'''' + I_2$. The alternatives $Fe^{\cdot\cdot} + I \to Fe^{\cdot\cdot\cdot} + I'$ and $FeCy_6''' + I \to FeCy_6'''' + I^{\cdot}$, followed by $I^{\cdot} + I' \to I_2$, are possible. The essential assumption is that reaction between acceptor and I_2' or I takes place far more rapidly than reaction 6.

Reaction with Potassium Oxalate.—Here the chain reaction is as proposed by Berthoud and Bellenot and by Dickinson and Ravitz, *i.e.* we have the additional reactions—

$$I + C_2O_4'' \to C_2O_4' + I' \qquad . \qquad . \qquad . \qquad (7)$$
$$I_3' + C_2O_4' \to 2CO_2 + 2I' + I \qquad . \qquad . \qquad (8a)$$
$$I_2 + C_2O_4' \to 2CO_2 + I' + I. \qquad . \qquad . \qquad (8b)$$
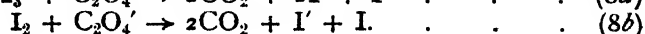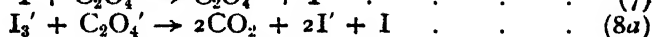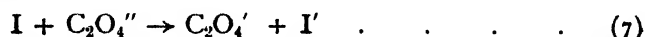
the I atom being the catalyst, and the chain being broken by (6). The necessary additional assumption is that $k_7[C_2O_4''] \gg k_{6b}$ [I] or its equivalent. The relations between $k_7[C_2O_4'']$, k_4 and k_3 [I'] are immaterial. The final equation—

$$Rate = \frac{k_7 [C_2O_4'']}{K_3 [I']} \cdot \sqrt{\frac{k_1 [\Sigma I_2] I_0}{k_6}}$$

merely differs from those of previous authors in that, whereas the latter only hold good for solutions containing an excess of KI sufficient to make the ratio $[I_3']/[I_2]$ large, the present expression should be valid independently of the amount of KI present.

Reaction with Potassium Nitrite.—The additional reactions required here are

$$OH + NO_2' \rightarrow OH' + NO_2 \qquad . \qquad . \qquad . \qquad . \qquad (9)$$
$$2NO_2 + H_2O \rightarrow 2H^{\cdot} + NO_2' + NO_3', \qquad . \qquad . \qquad (10)$$
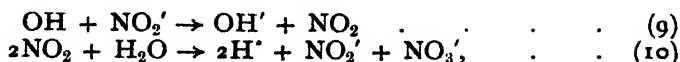
and the final expression becomes

$$\text{Rate} = \frac{k_1 k_4 k_9 I_0 [\Sigma I_2][NO_2']}{k_3[I'](k_9[NO_2'] + k_5[I']) + k_4 k_9[NO_2']},$$

differing in form from the equation deduced by Berthoud and Berger in that the latter lacks the second term in the denominator, and of course also holding for solutions weak, as well as for those strong, in KI.

Berthoud and Berger give certain data to which it is possible to fit the above formula. Thus, they find γ to be 0·045 for blue light and for a solution 0·1 N. KI + 1·0 N. KNO$_2$. Moreover, they state that the ratio k_9/k_5 (or rather the ratio of the velocity constants of the corresponding reactions postulated by them) appears to be 0·059, and they quote a whole series of relative velocities obtained experimentally with various solutions of KNO$_2$ and KI. With our mechanism, putting k_9/k_5 as 0·06, the value of γ quoted would be consistent with a value of 80 for h_3/k_4. For, assuming the efficiency of (1) to be unity, one would then have

$$\gamma = \frac{0·06}{8(0·06 + 0·1) + 0·06}$$

$$= \frac{0·06}{1·28 + 0·06} = 0·045.$$

Moreover, the modified formula fits the results quoted by Berthoud and Berger in much the same fashion as does their own. To illustrate this, we have calculated the relative velocities for the different reaction mixtures mentioned by them using (1) their formula and (2) the present one, employing the values of k_9/k_5 and h_3/k_4 given above. The results contained in Table III. show that there is little to choose between the two formulæ,

TABLE III.

Velocities: (a) found; (b) calculated B. and B.; (c) calculated A. and Y.

	KNO$_2$ 0·125 N.	KNO$_2$ 0·5 N.	KNO$_2$ 2·0 N.	
KI 0·2 N	0·132	(0·512)	1·43	(a)
	0·142	(0·512)	1·48	(b)
	0·143	(0·512)	1·45	(c)
KI 0·1 N	0·532	2·00	5·32	(a)
	0·547	1·81	4·31	(b)
	0·547	1·77	4·04	(c)
KI 0·05 N	1·84	5·04	11·17	(a)
	2·05	5·91	11·19	(b)
	2·00	5·43	9·60	(c)

even as actually employed, and indeed it only needs slight modifications in the relative values assigned to the different velocity constants to improve distinctly the degree of coincidence between actual experiment and the values calculated on our suggested mechanism.

We have been led to propose the intervention of OH groups, as opposed to HIO molecules, in the I$_2$ − KNO$_2$ reaction, for two reasons. The first

is the great difficulty of reconciling the reaction $I + I + H_2O \rightarrow HIO + H^{\cdot} + I'$, followed by $HIO + I' \rightarrow OH' + I_2$, a sequence which results in the removal of I atoms from the system, with the experimental data, qualitative and quantitative, of the KNO_2 and $K_2C_2O_4$ reactions. The second point is one to which Dr. D. W. G. Style drew our attention. The concentrations of both I_2' and I molecules in uninsolated aqueous solutions of iodine are quite negligible, and hence their production by light is consistent with a photochemical reaction of appreciable rate. On the other hand, HIO is already present, in definite though low concentration, in all such solutions before insolation (*e.g.* a rough calculation gives a figure of the order of $10^{-6} - 10^{-7}$ *M*. in the solutions used in our experimental work), and this concentration cannot be raised very much by irradiation, taking into account the assumptions necessarily made regarding the relative velocities of the different partial processes. It is therefore difficult to imagine the reaction $HIO + NO_2' \rightarrow NO_3' + H^{\cdot} + I'$ taking place to any extent in light, unless the freshly formed HIO molecules, arising from the action of I atoms on water, are endowed for an appreciable space of time with some activation energy, a further assumption which one would wish to avoid if at all possible.

The assumption of the intervention of OH groups appears to us to avoid these two difficulties. One point, however, remains unexplained and, in absence of further experimental data, must be looked on as a serious objection to our hypothesis. According to Berthoud and Berger, the T.C. for the reaction in yellow light is only 1·30 between $35^{\circ} - 45^{\circ}$ C. Neglecting any difference in extinction coefficient over this temperature range, this figure must represent the T.C. of

$$\frac{k_4 k_9}{k_3[I'](k_9[NO_2'] + k_5[I']) + k_4 k_9[NO_2']}.$$

From the nature of processes 3, 5 and 9, their activation energies would be expected to be relatively low, that of (9) being probably somewhat greater than the others. On the basis of the relative values already assigned to the different velocity constants, and without quite unlikely further assumptions, a T.C. of 1·30 in yellow light can only be explained on the supposition that the T.C. for process 4, and hence its activation energy, are also low. Such a conclusion is certainly in qualitative agreement with the assumption that the excess energy liberated in (1) is available for reaction 4, but even then it would appear probable that the net activation energy required in yellow light would be considerable. In default, however, of more detailed data on the effects of concentration and frequency on T.C. and γ, any further discussion of the point is premature.

Summary.

1. Experiments are described on the effects of intensity, temperature and frequency on the reaction between $K_2C_2O_4$ and I_2 in aqueous solution, employing monochromatic light.

2. In confirmation of previous workers, the velocity was found in every case to vary as the square root of the intensity.

3. The temperature coefficient was found to rise rapidly for shorter wavelengths with unstirred solutions. If the latter were stirred, this behaviour largely disappeared.

4. The quantum efficiency, depending on the method of comparison adopted was found either to increase with increase of wavelength, or else to pass through a maximum in the green.

5. Explanations are given for the anomalies noted under (3) and (4).

6. An attempt is made to deduce a mechanism which, with appropriate

modifications, will explain consistently the various known aqueous iodine photo-oxidations.

The experiments described in this paper were carried out during the session 1927-1928. The glass cells and filters, as also the thermopile, potentiometer and auxiliary electrical apparatus, were purchased out of grants made to the laboratory by Brunner, Mond & Co., Ltd., and by Imperial Chemical Industries, Ltd. The junior author (K.W.Y.) also wishes to acknowledge his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant received whilst a student-in-training.

University of London,
King's College.

GENERAL DISCUSSION.

On Part III., Paper 5.

Professor A. Berthoud (*Neuchatel*) said : I have been very interested in the work of Professor Allmand and Mr. Young on the photo-chemical reaction between iodine and potassium oxalate. I ought to say that measurements I have made recently upon the velocity of this reaction carried out in the dark have not confirmed the results given previously by Dhar, and by Bellenot and myself. The velocity of this reaction is approximately proportional to the concentration of the oxalate and to the square root of the concentration of iodine. From this we may conclude that the mechanism of the reaction is the same for the thermal and for the photo-chemical reaction, and the additive law cannot be applied in this case

The conception we have proposed in view of the researches we have carried out with Mr. Bellenot on the photo-chemical reaction satisfactorily accounts for all the observed facts. In the interpretation of the action of iodine on potassium nitrite however, we have come across difficulties due, on the one hand, to what we have supposed to be the action of light in dissociating the molecules I_2 but not the ions I_3'. On this matter we have already expressed the opinion that, perhaps, this supposition ought to be abandoned. It has moreover always appeared doubtful to us, for it would be surprising that blue light should be incapable of dissociating the ions I_3', whilst red light can dissociate the molecules I_2. It appears to me, however, that it will be better, before abandoning the question altogether and seeking another solution, to get some further experimental figures. I recognise, however, that the process suggested by Dickinson and Ravitz and adopted by Allmand and Young appears to be actually more probable than the one we have put forward, although, too, the criticisms which have been put forward by different authors do not all appear to me to be justified.

As for the conception of Allmand and Young for the reaction between iodine and potassium nitrite, I confess I am not entirely satisfied. The intervention in the phenomena of the intermediate compound OH seems to me doubtful. Moreover, Allmand and Young only look upon it as a working hypothesis. From this point of view, naturally, it is worthy of attention but, in this case more particularly, we must await further experimental research before drawing any conclusions.

Professor A. J. Allmand (*London*), in reply, said : It is of interest to note the new results of Professor Berthoud on the subject of the thermal

reaction between iodine and potassium oxalate, and it is probable that the corresponding method of correcting for the dark reaction would make a perceptible difference in those of our measurements in which the observed photo-reaction was low.

We are of course in agreement as to the desirability of further work on the $I_2 - KNO_2$ reaction.

A COMPARATIVE STUDY OF THE PHOTOGRAPHIC PROCESS IN DIFFERENT EXPERIMENTAL CONDITIONS.

By Professor Dr. John Eggert, *Leipzig.*

From the Wissenschaftlichen Zentrallaboratorium der Photographischen Abteilung der I. G. Farbenindustrie Aktiengesellschaft (Agfa).

Numerous researches have already been made towards the elucidation of the photographic process with its manifold details, and in many places further work, bearing on the present problem in different directions, is in progress. The present review will endeavour to compare definite viewpoints of the photographic process. The aim of the comparison is to obtain a uniform conception of the processes taking place. For this purpose, we first study the primary process (illumination only), that is the action of different kinds of radiation on photographic emulsions, then the corresponding secondary process (illumination, including development), next the shape of the density curve, the desensitisability of the film for different radiations, the influence of temperature during irradiation, and finally the photographic behaviour of some endothemine silver compounds which have not been used technically.

1. The Primary Process.

The primary process, which takes place on illumination of photographic emulsions, is usually interpreted to be the liberation, by the radiation, from the crystal lattice of the silver compound, of electrons which afterwards rearrange, so that after irradiation silver and bromine atoms remain.[1] To test this "silver nucleus theory" of the latent photographic image from energy considerations, the emulsion was illuminated with definite radiation, the part of the active absorbed energy was determined, the quantity of the photochemically changed substance was estimated by chemical analysis, and finally the number of energy quanta absorbed was compared with the number of silver and bromine atoms formed.[2] It was found that, to one absorbed quantum of energy corresponds, for light ($\lambda = 436\ m\mu$) about 1 silver atom, for X-rays ($\lambda = 0.5$ Å.) about 1000, and for α-particles about

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[1] K. Fajans in J. M. Eder, *Handb. Photogr. II*, 1, p. 633, 3rd ed., 1927; F. C. Toy, *Proc. 7th Intern. Congr. Phot.*, p. 14, Cambridge, 1929; F. C. Toy and G. Harrison, *Proc. Roy. Soc.*, A 127, 613, 629, 1930; S. E. Sheppard, *Industr. Engin. Chemistry*, 22, 555, 1930, where further references are given.

[2] J. Eggert and W. Noddack, *Berl. Ber.*, 39, 631, 1921; J. Eggert, *Z. Elektr.*, 32, 491, 1926; W. Nernst and W. Noddack, *Berl. Ber.*, 110, 1923.

50,000. In isolated cases it was also shown that, besides the silver atoms, the equivalent numbers of halogen atoms (measured as the secondarily formed ions) are produced.[3] Further, in the case of single crystals of silver halide, the latent image shows itself by colour change, and again gives evidence that—for light—each absorbed quantum $h\nu$ corresponds to the formation of about one " colour centre." [4] For these experiments (with the exception of the last-named) one cannot use such weak illuminations as in the normal photographic process, greater energy being necessary in order to carry out the chemical analysis afterwards. All these experiments show that the size of the quantum is the determining factor for the number of elementary processes. For light quanta the Law of Photochemical Equivalence holds approximately ; for X-rays, the energy quantum appears to be used for the formation of a large number of photochemically active electrons ; [5] for α-particles a similar process takes place even more frequently, owing to the larger quantum.

2. The Development.

The second part of the photographic process consists of the development, in which—neglecting the few particles which form the fog—only those silver halide grains are reduced which have been affected by the radiation. In this case the question also arises as to how the final state—the number of developed silver grains—depends on the size of the quantum of radiation. To answer this question, the emulsion must be irradiated with known energy, using, however, very much less than before. After the development of the emulsion, the numbers of reduced grains in both the illuminated and non-illuminated parts are counted and the difference between the numbers per unit area is compared with the number of quanta absorbed.

The track of each α-particle is a chain of silver grains, the number of which varies between 3 and 15 according to the experimental conditions. The same holds for H-particles.[6] For X-rays there is about one developed silver grain for each absorbed quantum.[7] For light too—according to the statistics of the quanta striking the emulsion—one absorbed quantum may correspond to one developed grain. On the whole, however, this case seldom arises, apparently only when the primary process which starts the development, has taken place at the surface of the grain, because it is only there that the developer has access. The ratio of the number of developed grains to the number of absorbed light quanta is about the same as the ratio of the number of silver halide molecules on the surface of a grain to the number inside, *i.e.* about $1 : 300$.[8] In the case of the action of X-rays on the grain this topographic condition need bear no relation to the following development process, because obviously the formation of 1000 atoms in a grain will always be sufficient to cause development.[7] The same holds true for the action of α- and H-particles, which on passing through the grain form sufficient active centres on them to ensure development.

[3] J. Eggert and W. Noddack, *Proc. 7th Intern. Congr. Phot.*, 39, Cambridge, 1929 ; E. Mutter, *Z. wiss. Phot.*, 26, 193, 1928, P. Feldmann, *Naturwiss.*, 16, 530, 1928.
[4] R. Hilsch and R. W. Pohl, *Z. Physik*, 64, 606, 1930.
[5] R. Glocker, *Z. Physik*, 43, 827, 1927 ; 46, 764, 1928 ; R. Glocker and O. Risse, *Z. Physik*, 48, 845, 1928 ; P. Günther, H. D. v. d. Horst and G. Cronheim, *Z. Elektrochem.*, 34, 617, 1928 ; P. Gunther and G. Cronheim, *Z. physik. Chem.*, B 9, 201, 1930.
[6] M. Reinganum, *Physik. Z.*, 12, 1076, 1911 ; M. Blau, *Sitzungsber. Akad. Wiss. Wien IIa*, 139, 327, 1930.
[7] J. Eggert and W. Noddack, *Z. Physik*, 43, 254, 1927 ; 51, 796, 1928.
[8] J. Eggert and W. Noddack, *Naturwiss.*, 15, 57, 1927.

3. The Density Curve.

By the density curve of a photographic emulsion is meant a curve which shows the amount * of (developed) blackening, d, as a function of the quantity of energy (intensity is multiplied by the illumination time, t, or number of absorbed quanta) active during the irradiation. The form of the density curve depends on the kind of radiation used. In Fig. 1 such curves are drawn for the same emulsion in such a way that under chosen conditions of illumination, *e.g.* 32 sec., the same density $d = 0·5$ is obtained ; this corresponds to point P in the diagram. If now, keeping the conditions of illumination otherwise the same, one determines the dependence of the density on time of illumination (correcting for the fog and adjusting the time scale) curves I and II are obtained ; curve I represents the action of α- and X-rays, II that of blue light. One notices, that the
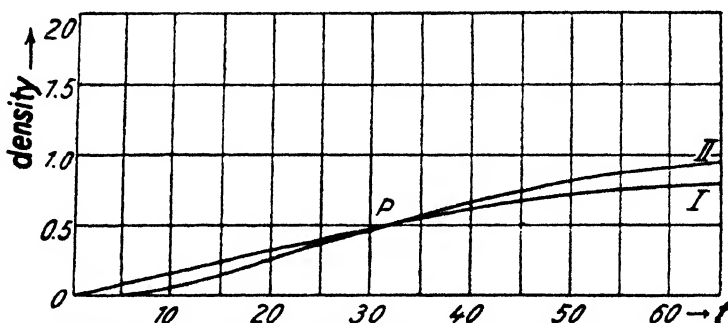
FIG. 1.—The density curves for X-rays and light plotted against energy (time) of illumination.

rays act in a different way on the emulsion, since for α- and X-rays the blackening is proportional to the energy, whereas for light a more than proportional increase of the curve is observed. This behaviour can be understood from earlier considerations since, *e.g.*, in the case of X-rays each incident quantum makes one new grain capable of being developed, and, as is well known, the density is proportional to the number of grains producing it, so that the density must also be proportional to the energy, at any rate so long as the illumination is not so strong that more than one quantum or α-particle hits a grain.[9] In consequence of this comparatively simple relationship, one is able to obtain a numerically accurate equation for the density-curve I (for α- and X-rays) given in Fig. 1 [10] this is :

$$d = d_0(1 - e^{-kt}),$$

where d is the density corresponding to time t, d_0 is the maximum density possible, and k a constant depending on the conditions of illumination and the type of emulsion. Amongst other things, k depends on the grain size, which enters as a factor of about $m^{2/3}$ [m = mass of a grain].[11] This formula holds exactly for α-rays, approximately for X-rays, because the latter,

* By definition $d = \log_{10} I_0/I$, where I_0 is the intensity of incident light during the measurement and I the intensity transmitted through the emulsion.
[9] W. Friedrich and P. P. Koch, *Ann. Physik*, **45**, 399, 1914 ; R. Glocker and J. Traub, *Physik. Z.*, **22**, 345, 1921 ; W. Bothe, *Z. Physik*, **8**, 243, 1922 ; A. Bouwers, *ibid.*, **14**, 374, 1923.
[10] The Svedberg and Andersson, *Photogr. J.*, **61**, 1921 ; The Svedberg, *ibid.*, **62**, 310, 1922 ; *idem, Kolloid-Chemie*, Leipzig, 1925, pp. 60-71 (translated by H. Finkelstein).
[11] J. Eggert, *Z. Elektrochem.*, **63**, 750, 1930.

especially for high illuminations, and also in other ways, show a certain relationship to light rays.

For light, the derivation of a correspondingly simple equation is not possible, since in this case other quantities besides the radiation determine the possibility of development of the grain. The superproportional increase of curve II suggests that the nucleus which starts the development is formed in the case of light, not only through the action of radiation, but that certain foreign substances, already present on the grain-surface before illumination, are taking part. Such "ripening" substances may be, on the one hand, metallic silver formed during the ripening process through reduction by the binding material or its contaminations, or, on the other hand, sulphur containing silver compounds, which are also thought to be formed during ripening.[12] These "ripening nuclei" now act as centres for the coagulation of the silver atoms formed by the light and build with them the development centres from which the further reduction of the whole grain in the developing liquid proceeds to completion.[13] Exactly how the nuclei are formed from the "ripening silver" and the silver produced by the light, is quite unknown; it is, however, certain that this coagulation process can explain the various anomalies of the photographic process (Schwarzschild-effect, intermittent effect, etc.) in a somewhat unforced manner.

4. Desensitisation.

The sensitivity of a photographic emulsion can be decreased by pre-treatment with certain substances (solutions of chromic acid, pinakryptol-dyes, etc.); this desensitisation effect, as is known, makes it possible to develop the emulsions in bright light.[14] It is found that the power of an emulsion to be desensitised (for equal pre-treatment) is different for different kinds of radiations, and in general the following rule holds : the greater the energy of the quantum of radiation, the less will be the influence of the desensitiser.[15] Therefore, the desensitisation of the emulsion is usually impossible for α-rays, difficult for X-rays and easy for light. It seems, nevertheless, as if, under certain circumstances, the properties of the grain can be changed so extensively by the desensitising bath that the action of high-energy radiation is also weakened.

5. The Influence of Temperature on the Primary Process.

With regard to the influence, which the temperature of the emulsion during the illumination has on the photographic effect, characteristic differences are shown by the different kinds of radiation. If we observe only in a temperature range in which no irreversible changes take place, and, therefore, no increase in sensitivity occurs through further ripening by the action of heat, we obtain the following picture (Fig. 2), which shows schematically the result of a great number of experiments on different kinds of emulsion.[16]

[12] This was established in 1925 simultaneously by: S. E. Sheppard and Punnet (J. M. Eder, *Handb. d. Photogr.*, II, 1, 3rd ed., p. 471); R. Luther and E. Mankenberg (Mankenberg, *Diss.*, Dresden), and O. Matthies, W. Dieterle, P. Wulff and B. Wendt (*D.R.P.*, 464, 450; 458, 286; 463, 286; 467, 179).
[13] The historical development of the theory is treated in J. Eggert and J. Reitstötter, *Z. wiss. Phot.*, 24, 350, 1927.
[14] Luppo-Cramer, *Negativ-Entwicklung bei hellem Lichte*, Leipzig, 1922.
[15] W. Meidinger, *Z. physik. Chem.*, 144, 89, 1925; S. E. Sheppard and A. P. H. Trivelli, *Phot. J.*, 66, 505, 1926.
[16] J. Eggert, *Ergebn. techn. Röntgenkunde*, Bd. II., 127; *Akad. Verl.*, Leipzig, 1931 (in the press; from experiments of Dr. F. Luft-Leipzig).

For equal quantities of energy, α-particles give a density independent of temperature (Curve I), X-rays give a density increasing slowly with the temperature (Curve II), a fact which is sometimes used in making structure diagrams;[17] in the case of light the temperature of the emulsion has an essential influence on the value of the density. The flat maximum is reached at about $- 20°$ C. (Curve III). The explanation of these phenomena is still unknown. Since an effect of development is excluded, and also since one cannot assume that the absorption process, as such, is influenced by temperature, the only assumption remaining is that the secondary processes taking place after the absorption, cause the observed temperature effect. There are two possibilities, either a change in the reverse reaction, or a change in the process of nucleus formation. In the first case, one would have to assume that a fraction of the atoms formed, varying with tempera-
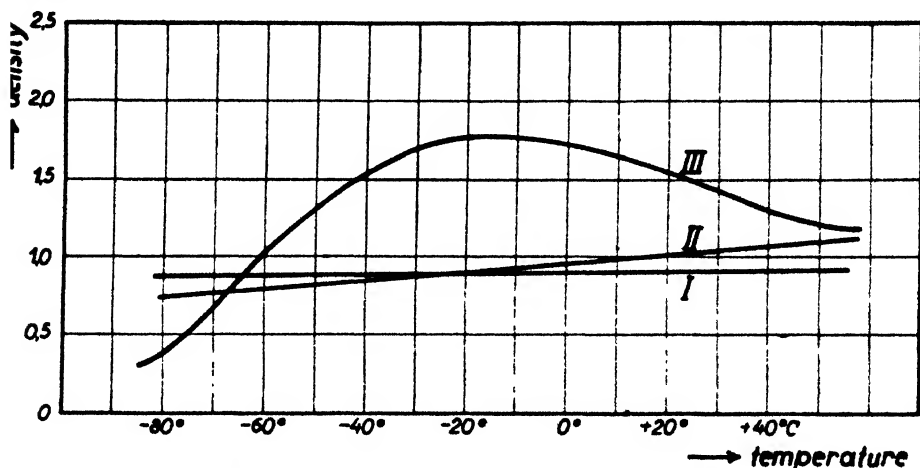
FIG. 2.—Schematic representation of the dependence of the density of photographic emulsions on the temperature during irradiation with constant energy.

I α-Rays; II X-Rays; III Light.

ure, recombines to silver halide, and in the other, and perhaps more probable case, that it is not a chemical change which is dependent on temperature, but the physical process of the formation of the nuclei, i.e. the coagulation of atoms into groups which later are catalysts in the development.

5. The Photographic Behaviour of Endothermic Silver Compounds.

Finally, we have to differentiate between the action of radiation on different silver compounds.[18] One would expect the biggest effect on comparing exothermic substances, e.g., halides, with endothermic compounds, e.g., silver azide, silver acetylide, and silver oxalate. For this purpose we have prepared emulsions of these substances of equal silver content and very similar degree of dispersion, in gelatine as binding material, and convinced ourselves that the absorption of the films is of the same order of magnitude for $AgCl$, AgN_3, Ag_2C_2 and $Ag_2C_2O_4$. According to the theory of chain reactions a stronger photographic effect might possibly occur in

[17] F. Ebert, Z. anorg. Ch., 179, 279, 1929.
[18] Unpublished experiments of Dr. H. Arens-Dessau and Dr. F. Luft, Leipzig.

the case of endothermic compounds than in the case of exothermic, especially when using energy-rich radiation. Actually such an effect has not yet been found. If one irradiates the four emulsions mentioned simultaneously with equal amounts of energy of visible light, X-rays or α-rays, practically the same photographic effect is observed for each radiation on the four kinds of emulsion. Moreover it is noticed, as has long been known for silver azide,[19] that the photographic properties of the above emulsions are quite unsuited for technical use. In a few cases the experiments showed very peculiar features: While in the case of silver bromide and silver chloride the (active) spectral absorption corresponds to the spectral sensitivity of the emulsion, in the case of the endothermic silver compounds an essentially different state of affairs appears to exist. In addition the primary reaction (carried out under equal irradiation conditions) appears to show that it is not the *energy* of the compound which is important for the photochemical reaction so much as the photoelectric and *kinetic* behaviour of the substance.

Summary.

1. The magnitude of the *primary* effect in the photographic process, measured by the number of silver atoms formed per quantum of radiation, increases with the size of the quantum of energy.

2. The value of the *secondary* photographic effect, measured by the number of developed silver bromide grains, also increases similarly.

3. A corresponding conclusion may be drawn from the course of the *density curve*.

4. The *desensitisability* of the emulsion decreases in the order light, X-rays, α-rays.

5. The temperature which prevails for the irradiation is without influence on the photographic effect in the case of α-rays, has little influence for X-rays, while for light a marked dependence is observed.

6. Special features are observed on making such comparisons for endothermic silver salts, such as AgN_3, Ag_2C_2, and $Ag_2C_2O_4$.

[19] J. Beck, *Z. Wiss. Phot.*, **14**, 105, 1915.
[20] R. H. Lambert and W. C. P. Wightman, *J. Physical Chem.*, **31**, 1249, 1927.

THE LATENT PHOTOGRAPHIC IMAGE. NEW METHODS OF INVESTIGATION AND RESULTS.

By Fritz Weigert (*Leipzig*).

From Experiments by Dr. F. Stiebel. *Translated by Dr. Wilfred Gallay.*

In the following remarks we shall restrict ourselves to the effect of light on photographic silver halide emulsions with development, excluding from consideration the photographic effect of Röntgen and corpuscular rays.

The first proposal to represent the *photographic properties* of an emulsion quantitatively by means of the dependence of the density or extinction of the developed silver on the logarithm of the acting amount of light, *it*, was made by Hurter and Driffield. The "Characteristic Curve" has in general the well-known S-shaped form, shown in Fig. 1. This function represents simultaneously the *photochemical properties* of the photo-sensitive system,

when one considers the total course (including the exposure and the development) as the photochemical process.   For it really does not matter whether (as in the simple photoprocesses) the real primary process and the succeeding chemical processes follow one another so closely that they cannot be separated experimentally, or whether, as in photography, the partial
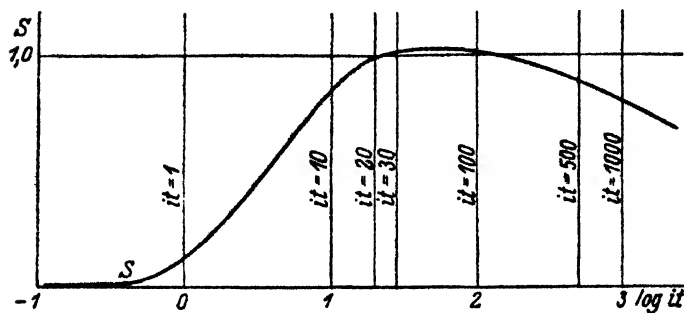
FIG. 1.

processes are widely separated from one another in time of occurrence.

For the graphical representation of the photochemical process, we may replace the density D by the practically proportional amount of silver Ag for the ordinate and the logarithmic division of the abscissa by a linear scale of the amount of light (Fig. 2, curve A).   The dotted line B represents the course of a normal photochemical reaction as formulated by the Einstein Equivalent law with
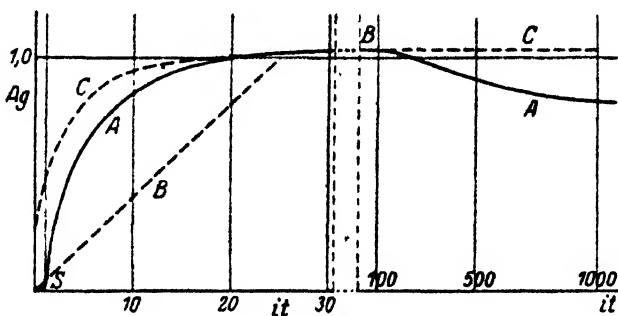
FIG. 2.

constant light absorption; one immediately recognises the completely anomalous course of the photographic process, for which the appearance of a threshold value " S," is characteristic.   The velocity of reaction is accordingly strongly dependent upon the amount of light, and from Fig. 3 (in which the differential quotient A' of the function A, $dA/d(it)$ in Fig. 2, is represented), it appears that the velocity of photographic action A' is at first very small, then rises steeply,
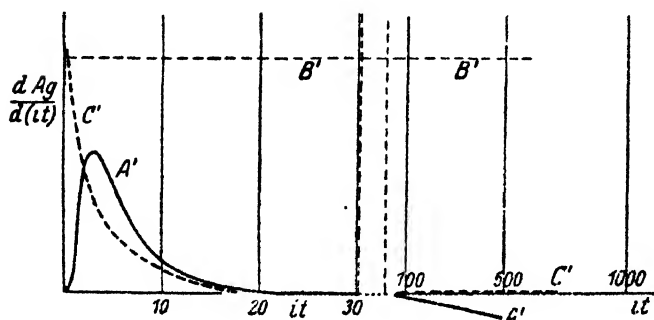
FIG. 3.

passes through a maximum and then continually decreases.   In the field of solarisation, the velocity of the formation of developed silver becomes even negative; that is, with increasing exposure the density no longer increases, but actually decreases.

For the photographic process the light-absorption is constant, since, during the exposure and the formation of the " latent image," the system is not appreciably changed optically. A normal photochemical reaction proceeds with constant velocity according to curve B' under these conditions, independent of the time of exposure.

In order to study these relationships more closely we have made use of the following method. We know from previous observation that, by the exposure of transparent photographic layers to linearly polarised light, the developed silver becomes dichroitic and anisotropic. This effect, only recently known, we termed " Induced Photo-Dichroism." For the amount of the anisotropic developed silver, the same relationships hold as given in Figs. 1 to 3 in curves A and A'. If, now, we excite the same part of the plate with natural and polarised light successively, so that later two kinds of " latent image," one isotropic and one anisotropic are developed simultaneously we can, by measuring the dichroism of the developed silver, investigate separately the photographic effect of the two kinds of light. Thus we determine whether or not the two latent images have affected each other. Such an experiment was not possible before the discovery of induced photodichroism, since it could no longer be recognised from the developed silver, through which sort of light the latent image had been formed.

We carried out a very great number of experiments, with mixed excitations in different combinations for the colour and type of polarisation of the exciting light, using different chemical and physical developers.[1]

We will here discuss only a few cases which appear to be of importance in relation to our knowledge of the latent image. The special method of measurement has already been fully described.

Five positions on strips of the Imperial Gaslight plates were exposed for the same length of time to the excitation of red polarised light and then these positions were exposed to natural light for 0, 2, 8, 30 and 120 seconds respectively. All of these comprised one group.[2] Four such groups were prepared, differing only in the times of $\nearrow$, namely 2, 8, 30 and 120 seconds. Furthermore, each group contained two series, in one of which excitation was first by natural and then by polarised light (O, $\nearrow$) and in the other the reverse ($\nearrow$, O). Development was carried out either with a dilute physical para-phenylene-diamine developer (with addition of sulphite) before fixation, or with dilute iron oxalate developer, since it was found after numerous experiments that these two yielded the simplest results. In the main, however, the results with all developers are practically the same.[3]

Since dichroism signifies the varied transparencies of the developed silver in two planes of vibration of light at right angles to each other, it can be quantitatively determined by means of the logarithmic relationship between the intensities of the light allowed through in the two planes.

$$D = \log \frac{I_1}{I_2}.$$

[1] The formation of developed or induced photodichroism is a quite general phenomenon. It appears in silver chloride, silver bromide and silver iodide emulsions and in mixtures of these. The one condition to be fulfilled is of a purely optical nature. The exposed layer must be as transparent as possible, in order that the polarised light be not depolarised by diffuse dispersion through turbidity-causing silver halide crystals. The only commercial plates sufficiently transparent were Imperial-Gaslight Dry Plates, Warm Tone, and a Lumière Diapositive plate. The other different emulsions were prepared in the laboratory.

[2] Exposure to polarised light will be designated by $\nearrow$ and that to natural light by O.

[3] Fuller details will be published later.

If I_1 is the intensity of the light allowed through in the optical axis of the photoanisotropic system (this axis lying, according to previous experiments, in the plane of vibration of the electrical vector of the exciting polarised light), and I_2 the intensity in the plane of vibration at right angles to the optical axis, then the photodichroism is given a positive sign provided that I_1 is greater than I_2. In the reverse case, the sign is negative.

If we designate the extinction or density of the dichroitic developed silver in the two chief planes by E_1 and E_2, then the dichroism is

$$D = E_2 - E_1.$$

Further $E_1 < E_2 \rightarrow + D$ and $E_1 > E_2 \rightarrow - D$.

In the case of excitation with red polarised light, D is almost always negative, E_1 being accordingly greater than E_2.

In Tables I. and II. are shown the very clear effects for excitation by red polarised light ($\nearrow$), the additional exposure (○) being to blue, green and red. The light was filtered through colour filters whose breadths of transparency did not overlap. The vertical columns of the tables contain the results with the *same* polarised excitation; there being four groups according to the time of exposure to the polarised light. The series on the left side of the tables represent natural pre-exposure and those on the right, natural after-exposure. *The time for development was in all cases the same (3 min.).*

TABLE I.—Induced Photodichroism (D).

	Blue: ○ Red: ↗				Red: ↗ Blue: ○			
	2″.	8″.	30″.	120″.	2″.	8″.	30″.	120″.
0	− 0·18	− 3·90	− 11·80	− 13·65	− 0·27	− 4·50	− 11·85	− 14·7
2″	− 0·66	− 4·35	− 12·45	− 13·32	− 0·65	− 4·57	− 13·35	− 13·89
8″	− 1·12	− 5·70	− 11·1	− 13·65	− 1·36	− 6·07	− 13·5	− 16·0
30″	− 2·07	− 5·85	− 10·32	− 13·80	− 2·19	− 8·1	− 13·89	− 16·65
120″	− 2·02	− 5·25	− 9·8	− 14·25	− 1·93	− 6·96	− 12·08	− 17·85

	Green: ○ Red: ↗				Red: ↗ Green: ○			
	2″.	8″.	30″.	120″.	2″.	8″.	30″.	120″.
0	− 0·21	− 4·08	− 9·38	− 14·25	− 0·22	− 3·38	− 11·17	− 13·9
2″	− 0·33	− 3·96	− 8·77	− 14·1	− 0·22	− 4·50	− 11·52	− 13·9
8″	− 0·60	− 4·5	− 8·32	− 13·65	− 0·55	− 4·55	− 11·8	− 13·6
30″	− 1·11	− 4·83	− 8·77	− 13·0	− 1·62	− 6·45	− 12·9	− 14·8
120″	− 1·09	− 4·55	− 7·8	− 15·60	− 1·87	− 7·35	− 11·5	− 5·58

	Red: ○ Red: ↗				Red: ↗ Red: ○			
	2″.	8″.	30″.	120″.	2″.	8″.	30″.	120″.
0	− 0·15	− 3·15	− 11·85	− 13·88	− 0·24	− 4·13	− 11·78	− 13·89
2″	− 0·21	− 3·30	− 11·62	− 13·8	− 0·30	− 4·21	− 12·3	− 13·4
8″	− 0·51	− 4·02	− 11·18	− 12·72	− 0·36	− 4·08	− 10·94	− 12·96
30″	− 1·05	− 4·5	− 10·8	− 13·12	− 0·59	− 3·78	− 9·22	− 11·7
120″	− 1·14	− 4·2	− 8·17	− 12·6	− 0·75	− 3·16	− 5·92	− 9·55

TABLE II.—Average Increase of Photodichroism $\frac{\Delta D}{\Delta(it)}$ with Time of Exposure.

O ↗	Blue: O Red: ↗				Red: ↗ Blue: O			
	0-2".	2-8".	8-30".	30-120".	0-2".	2-8".	8-30".	30-120".
0	0·09	0·62	0·39	0·020	0·13	0·70	0·33	0·032
2"	0·33	0·62	0·39	0·010	0·31	0·66	0·41	0·006
8"	0·56	0·76	0·25	0·028	0·68	0·79	0·33	0·016
30"	1·04	0·63	0·21	0·039	1·1	0·99	0·25	0·032
120"	1·01	0.54	0·21	0·049	0·98	0·84	0·22	0·064

O ↗	Green: O Red: ↗				Red: ↗ Green: O			
	0-2".	2-8".	8-30".	30-120".	0-2".	2-8".	8-30".	30-120."
0	0·1	0·64	0·24	0·054	0·1	0·52	0·36	0·03
2"	0·16	0·60	0·23	0·06	0·1	0·7	0·36	0·015
8"	0·30	0·64	0·18	0·06	0·27	0·68	0·33	0·02
30"	0·55	0·61	0·18	0·04	0·8	0·81	0·28	0·021
120"	0·55	0·57	0·15	0·09	0·93	0·91	0·18	0·048

O ↗	Red: O Red: ↗				Red: ↗ Red: O			
	0-2".	2-8".	8-30".	30-120".	0-2".	2-8".	8-30".	30-120".
0	0·07	0·49	0·39	0·022	0·12	0·64	0·34	0·024
2"	0·1	0·51	0·38	0·024	0·15	0·64	0·37	0·012
8"	0·25	0·58	0·33	0·018	0·18	0·61	0·31	0·022
30"	0·52	0·57	0·28	0·025	0·30	0·54	0·24	0·027
120"	0·57	0·51	0·18	0·049	0·37	0·4	0·12	0·04

From Table I., we see that the negative dichroism of the developed silver is quite generally strengthened in the case of short polarised excitation ($\nearrow$ 2 seconds), by a pre- or after-exposure. We consider it particularly important that this strengthening occurs through *both* pre- *and* after-exposure to natural light. If it were so only in the case of *the natural pre-exposure*, it could be assumed that the layer becomes in this way "more sensitive" to after-excitation by polarised light. In that case, however, the same effect with natural after-exposure would not be understandable. We conclude from this state of affairs, in the first place, purely phenomenonologically, that these successively formed "latent images" do not exist simply side by side (as has been assumed in all previous conceptions as to the mechanism of the photographic process), but that they affect each other very strongly, since the developability of the first formed anisotropic image becomes strengthened by a natural after-exposure. With longer polarised excitations the field of over-exposure had already been reached and the effects were irregular.

If we calculate the average increase of the photodichroism with time of excitation from the figures of Table I. (experiments that must be extended to smaller linear time intervals) it may be seen from Table II. that in the case of *short* polarised excitation, a maximum value for this increase is reached asymptotically with increasing natural pre- or after-exposure,

particularly in the case of blue (Columns 0-2 seconds). The change of the dichroism with the change of time of polarised excitation *without natural additional excitation* runs through a maximum (1st horizontal series of the tables), just as is required by curve A′ in Fig. 3. With sufficient natural additional excitation, however, the velocity of this process continually decreases (5th horizontal series of the tables). This course of the phenomena represented in curve C′ is noticeable in all cases, being especially pronounced however in the case of short wave natural additional exposure.

We wish again to call attention to the importance of this hitherto unknown photographic phenomenon. In the comparable experiments (vertical columns of the tables) the polarised light acts for the same length of time on the plate. If later, on development, dichroitic silver is formed, the anisotropy can be caused *only by this polarised excitation*. The result to be expected upon the addition of natural light would be an increase of the total developed silver and also of the photographic density, but the amount of *dichroitic* silver ought not to be increased. The natural supposition, indeed, would be that there should be a diminution of the developed dichroism, since the mixed exposure corresponds in a certain sense to a radiation of a smaller degree of polarisation.

We find, on the other hand, that the dichroism is very much strengthened, in some cases to the extent of ten times, by the natural pre- or after-exposure. This can be interpreted by assuming that through natural additional exposure something occurs which causes the *anisotropic* latent image to become more strongly developable. Accordingly, the *latent anisotropic image*, after completion of the polarised excitation, is still open to influence *by other factors*, brought about by the natural light, in spite of the fact that the latter certainly possesses no particular orientation. The *chief factor* determining the *optical properties* of the developed silver is conditioned by the *form of vibration* of the light used for excitation. The amount of the developed dichroitic silver, in our case, however, can be increased during the same time of development, by another factor, added by the natural exposure.

In the developable photographic latent image, there are, accordingly, always at least two factors effective at the same time. These we wish to differentiate by the terms *Form-Factor* and *Activation-Factor*. The form factor stands in very close relation to the exciting light, by reference also to its *form* of vibration ; the latter may be either natural or polarised. However, the form factor alone does not condition the degree of developability. This can be initiated only by the activation factor, which we can strengthen, for example, by the aid of natural exposure. The limit of the amount of dichroitic developed silver so obtainable, is determined by the form factor alone. This limit is reached most quickly by the addition of short-wave natural light.

Now, such a dependence of increased dichroitic effect upon time of excitation has been known for some time in the simplest cases where photodichroism occurs. We may mention those of the photochloride emulsions, containing a solid solution of finely divided metallic silver in silver halide. The effect of polarised light on these materials was discovered some 12 years ago. These layers are *not developed ;* the originally noticeably coloured layer becomes *directly* photodichroitic by radiation with polarised light. This direct effect was differentiated, by the term *primary photodichroism*, from the previously described " developed " or *induced photodichroism*. At the same time, the photochlorides show an *adaptation to the colour of the exciting light*, and by analogy, the dichroitic effects may

be termed *adaptation to the orientation of vibration of the light.* The adaptations to both the orientation of vibration and to the colour proceed according to the functions diagrammatically shown in curves C and C′ of Figs. 2 and 3.

The steepest slope of curve C (Fig. 2) and the maximum velocity (Fig. 3, curve C′) are found at the start, and there is no trace of the "threshold value" designated by S in Figs. 1 to 3. Now, it is known by analysis that all photographic silver halide emulsions contain small quantities of finely divided silver, termed "Original silver" (*Ursilber*). Thus these emulsions must be considered as being photohalides containing only very small amounts of silver, and the "form factor" stands in very close relation to the processes which bring about the primary dichroism. We know that these processes are not chemical in nature, but consist of a mechanical transformation of the photochloride micellæ without increase in the amount of silver, these micellæ becoming anistropic through excitation with polarised light. The sensitivity to polarised light (and hence also to the form factor) of the primary dichroism of the photochloride, decreases *continually* with increasing time of exposure. (Curve C′ in Fig. 3.)

We can at this stage only conjecture as to the nature of the "activation factor." We are of the opinion that in some manner finely divided metallic silver is here involved. This supposition can be put to trial experimentally, since this hypothetical activation silver can be chemically removed by an oxidising agent. The developability should thereby be reduced. When the plate, after excitation with polarised light, was treated with chromic acid, no image could be developed with iron oxalate developer.[4] This well-known photographic experiment alone would not prove our idea of the co-operation of a form factor in the latent image formation. When, however, after the chromic acid treatment (before development) we expose the plate again to red *natural* light and then develop, we obtain dichroitic developed silver of *positive* sign, in contrast to the negative values of all previous experiments.

By means of this experiment it is proven that despite the fact that they are no longer developable after chromic acid treatment, the spots excited by polarised light still possess anisotropic properties; hence a "latent transformation" is still present. Only one component of the natural light used for the after-excitation was effectively absorbed, namely the one at right angles to the plane of vibration of the polarised light previously used. This, however, was to be expected, since according to Fig. 3, curve C′, the system had become much less sensitive in the plane of vibration of the primary exciting light and, consequently, the component of the natural light at right angles to this plane exerted the stronger action. Thus the layer was transformed into a *photochemical polariser*[5] through the pre-exposure and treatment with chromic acid, enabling it to divide natural light into its polarised components.

The inversion of the sign of the developed photodichroism from negative to positive described in this experiment, is analogous to one described by Albert some time ago, and later thoroughly investigated by Lüppo-Cramer. In the Albert-effect a plate under an object was exposed to ordinary light, treated with chromic acid and then exposed again to diffuse light. Upon development, there appeared not a negative but a positive image. In this case also the previously exposed spot, therefore, became less sensitive to

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[4] This developer was used, since it acts only on the micellæ and not on the silver-halide crystals. The experiments in connection with this problem will be published later.
[5] F. Weigert and F. Stiebel, *Naturwiss.*, **19**, 108, 1931.

the after-exposure. Our new experiment of the inversion of negative di-chroism to positive shows us that the pre-exposure does not lead to the formation of a new chemical substance which makes the silver halide less sensitive to further exposure, since the activity of such a substance could not be confined to only one plane of vibration.

We will now attempt to apply to the interpretation of our results, the micellar theory of the latent image proposed some time ago.[6] According to this idea, very many light quanta can be absorbed by a single micella. The latter is presumed to consist of silver halide, gelatine, original silver (*Ursilber*) and other components of the emulsion. By means of the absorbed energy, work is performed against the Van der Waals forces which hold the micella together. In the simplest case there occurs a " loosening " (*Auflockerung*)[7] the latter being anisotropic upon radiation with polarised quanta. This idea alone would explain the anomalous summation of effect of various light quanta, which affect each other in the same micella.

According to our recent experiments, however, the energy stored up in the micellæ is still insufficient for the introduction of the development process. For the latter, a catalyst is necessary and this catalyst we consider to be identical with the " Activation Factor " mentioned above. From the point of view of quantum mechanics, a high level of potential must be surmounted in order to make possible the reduction of the silver halide by the developer.

This obstruction is levelled by an *activation* in which atomic silver takes part, the activating silver atoms being already present in small amounts in every normal silver halide emulsion in the form of " original silver." This small quantity will be increased if, during exposure, the energy stored up in the micella is used for an " inner development " with the consequent reduc-tion of silver halide to atomic silver. This secondarily formed *photosilver* is produced by the natural pre- or after-excitation, and it is capable of ac-celerating the development of the anisotropic latent image formed in the same miscella by polarised excitation. If the silver·is dissolved out by chromic acid, the developability ceases. However, on a subsequent natural exposure, and consequent new production of the activation factor, develop-ment is again made possible. Moreover, this anisotropic development occurs preferentially in the direction of vibration at right angles to that of the primary exciting light, because in this plane the micellæ are less affected and hence remain more light-sensitive.

The total course of curves A and A' in Figs. 2 and 3 can now be ex-plained in a simple qualitative manner by the combined effects of the form and activation factors. According to our experiments, absolutely pure silver halide is not light sensitive. We consider the *Form Factor F* the real latent image. Its production is thus dependent on the amount of original silver and other sensitisers within the micellæ. It may probably be represented by a function

$$F = K(\text{I} - e^{-\alpha it})$$

corresponding to curve C of Fig. 2. K is here a factor bearing a relation to the effectiveness of the sensitisers, *it* is the amount of light radiated and a a constant. In the photographic emulsion however, the energy stored up in the micellæ is used to a continually increasing extent for internal develop-ment, with consequent increase of the activation factor A. The velocity of

[6] F. Weigert, *Z. wiss. Phot.*, **29**, 191, 1930.
[7] From the point of view of quantum mechanics also an inverse effect, a " tighten-ing " may occur with a certain probability in the micella (*cf.* F. Weigert, *Z. physik. Chem.* (B), **10**, 263, 1930.

formation of the activation factor A can be most simply represented by means of a linear function

$$\frac{dA}{dt} = K'F.$$

In this manner the threshold value S of Fig. 2 for the developability is attained and the reaction velocity increases autocatalytically. With further exposure the velocity of formation of the form factor $\left(\frac{dF}{dt}\right)$ approaches zero asymptotically, since the Van der Waals forces are continually lessened. The activation factor is increased at the expense of the stored-up energy and thus the form factor is decreased. Since the form factor determines the limit of the reduceable silver halide, the developability must continually decrease finally becoming negative in the field of solarisation.

In the case of such a large increase, the presence of activation silver may even be proved analytically. The experiments of Eggert and co-workers, showing that the developability of a photographic emulsion does *not* run parallel with the amount of analysable photo-silver confirm our conceptions.

Further general properties of the characteristic curve, for example the aberrations from the Bunsen-Roscoe Law, can readily be interpreted qualitatively on the basis of the combined effects of these two factors of the latent image. They will be more thoroughly discussed after the completion of the experiments now in progress in this field.

In conclusion, it might again be emphasised, that the new method of investigation of photographic processes is confined only to transparent special emulsions. We consider it justifiable and very promising, however, to extend our inferences to normal highly sensitive emulsions since our conceptions have served to provide an explanation of the very general form of the characteristic photographic curve. Further, our inversion of negative to positive dichroism after chromic acid treatment holds also for ordinary photographic emulsions in the inversion of a negative to a positive image.[b]

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[b] Further experimental details have been published meantime by F. Weigert and F. Stiebel in *Z. physik. Chem.*, **B**, **13**, 314, 1931, and *Z. Photogr.*, **31**, August, 1931.

SENSITISATIONS OF THE FIRST AND SECOND TYPES.

By Fritz Weigert* (*Leipzig*).

(*Translated by Dr. Wilfred Gallay.*)

We shall endeavour in the following pages to indicate in a somewhat cursory manner the possibility of differentiating between two charactertstic types of sensitisations, without going more closely into the special mechanism of sensitisation.

Sensitisations of the First Type.—In this type the sensitiser is present only in very small amounts, working as a photo-catalyst for a large number of reacting molecules. Its photo-chemical efficiency is very great and γ is much greater than 1. We may mention, as examples, the colour sensitisers of the photographic emulsions, mercury atoms in the experiments of Cario and Franck, Taylor, Marshall, and other investigators. One finds very commonly that, in these sensitisations, after passing an optimum point, the sensitising effect decreases with increasing concentration.

Sensitisations of the Second Type, on the other hand, require a large excess of the sensitiser. To this class belong, *inter alia*, sensitisations by chlorine, particularly the chlorine-ozone reaction. By a continuation of the investigation of the photo-chemical transformation of o-nitrobenzaldehyde into o-nitrosobenzoic acid, reported upon by Fräulein Dr. Brodmann and myself at the preceding photo-chemical meeting of the *Faraday Society*,[1] Fräulein Dr. Pruckner[2] has recently been able to show that acetone is a sensitiser of this second type. Upon repetition of the previously carried out measurements of γ for the wave-lengths 436, 405, and 366 $\mu\mu$, and extension by means of a new method to 313 $\mu\mu$, the remarkable value 0·5 was again found for all cases. Table I. embodies the results at 313 $\mu\mu$

TABLE I.

Concentration of Aldehyde Per Cent.	Average γ†.	L Aldehyde Per Cent.	L Acetone Per Cent.
2	·485 (3)	75	25
1	·500 (4)	67·2	32·8
0·5	·478 (5)	50·6	79·4
0·2	·538 (4)	28·9	81·t
0·1	·529 (2)	16·9	83·1
0·05	·444 (2)	9·2	90·8
0·02	·381 (2)	3·9	96·1

† The figures in brackets indicate the number of check experiments under the same conditions.

for various concentrations of the aldehyde. In this region, however, acetone already absorbs very strongly, and when the extinction constants of 22 for

* From experiments by Dr. Franziska Pruckner. See F. Weigert and F. Pruckner, *Z. physik. Chem., Bodensteinband,* 1931.

[1] *Trans. Far. Soc.,* **21**, 453, 1925.   [2] *Diss. (Leipzig),* 1931.

acetone and 45 for the aldehyde in 1 per cent. solution are inserted, the last two columns of the table show the proportions of the amount of light absorbed by the two components of the solution, $L_{ald.}$ and $L_{ac.}$

$$L_{ald.} = L_{total}\frac{E_{ald.}}{E_{ald.} + E_{ac.}}.$$

$$L_{ac.} = L_{total}\frac{E_{ac.}}{E_{ald.} + E_{ac.}}.$$

Despite the fact, then, that at small concentrations of aldehyde, only very little light is absorbed by the aldehyde itself, γ remains practically constant $= 0.5$. The energy must therefore be carried over by the acetone to the aldehyde, and hence acetone works as a sensitiser of the second type. The factor $\frac{1}{2}$ is here of particular interest, since it has already been found on several occasions and, moreover, this result seems to have a more general significance. Following the first case with o-nitrobenzaldehyde, Jäckh in my laboratory found the same factor for the transformation of anthracene to dianthracene.[3] Then Forbes and Leighton[4] observed the same value for the reaction of quinone with alcohol, and we find it now in the case of the activation of acetone. There are then four cases known, whose common property is that a complicated organic reaction is concerned.

We believe, moreover, that a sensitiser of the second type exists also *in the solid system* which we presume in the silver halide. The assertion I made a number of years ago, that very pure silver halide is not light-sensitive may now be considered as verified, according to newer experiments of other observers. In order to bring about the photo-chemical process, small amounts of impurities, defects in crystal structure or "loose positions" (Lockerstellen),[5] must be present within the crystal.

The experiments to hand distinctly favour the idea that in the parts of the spectrum where the silver halide itself strongly absorbs, the energy which in pure crystals is used only for heat production is chemically fully utilised in the presence of defects, etc. We have, therefore, again a sensitiser of the second type which carries its energy to the "light-sensitive" spots not, as in the cases of gases and liquids, through impacts, but by means of lattice vibration.

Coincidentally with the first short statement concerning this sort of sensitisation through silver bromide,[6] which may be of importance for photography, there appeared an investigation by Tomaschek pointing out the transfer of radiant energy to the phosphorescence centres in a similar way, and discussing the possibility of the transfer of these ideas to photo-chemical catalyses.[7]

We do not consider it to be out of the question that the sensitisations of the first and second types do not differ from one another from the standpoint of theoretical photo-chemistry, but we must not neglect to point out the very varied composition of light-sensitive systems which occur in practice.

[3] *Diss. (Leipzig)*, 1927 ; J. Weigert and W. Jackh, *Naturwiss.*, **15**, 125, 1927.
[4] P. A. Leighton and S. L. Forbes, *J. Amer. Chem. Soc.*, **51**, 3549, 1929.
[5] I presume that in these cases a "Micellar-loosening" takes place, and that the energy so built up is then secondarily changed into chemical energy. However, the special mechanism is not to be discussed here.
[6] F. Weigert, *Z. Wiss. Phot.*, **29**, 200, note 1, 1930.
[7] R. Tomaschek, *Z. Elektrochem.*, **36**, 738, 1930.

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physikalisch chemischen Instituts der Universität.

GENERAL DISCUSSION.

On Part III., Papers 6-8.

Dr. J. Y. Macdonald (*St. Andrews*) said: I wish to ask Dr. Eggert whether the silver oxalate he used was prepared with an excess of silver ion or of oxalate ion, and if he had noticed any difference in the behaviour of the salt according to which method was used.

I should also like to ask whether any experiments had been done in an oxygen-free atmosphere. Oxygen greatly retards the thermal decomposition of silver oxalate[1] and it is possible that it may have the same effect on the photo-chemical reaction.

Professor J. Eggert (*Leipzig*), in reply to Dr. Macdonald said: The preparation of all the emulsions had been brought about by an excess of oxalate or the other negative ions. This method must be used because an emulsion with excess of silver ion cannot be developed without fogging. The experiments were done in the free air. No special precautions were taken to ensure absence of oxygen.

Dr. W. Frankenburger (*Ludwigshafen*) said: Professor Eggert in his paper has estimated that on the average about 300 absorbed quanta are necessary to develop each silver bromide grain in a normal emulsion; he concludes that this relatively small energy yield is due to the fact that 299 silver atoms which were situated inside the grain during the primary process do not contribute to the process of development and that, on the average, only one silver atom is formed, this being on the surface of the grain, *i.e.* in a position necessary for development. I would ask whether this poor utility factor 1 : 300 cannot also be explained on the assumption that, although a considerably larger number of silver atoms are to be found at the surface of a grain, it is only necessary, in order to bring about development, to affect there a single atom, and that this is a necessary preliminary to affect a silver particle having a large number of atoms.

Professor J. Eggert (*Leipzig*), in reply, said: This question has naturally occurred to us and, as I venture to believe, the answer is as follows: In order to bring about the formation of a nucleus situated on the surface (with a view to development of a silver bromide particle) we do not in fact make use merely of *one* silver atom, but an aggregate of several atoms (not less than a certain minimum number) is necessary. These atoms will however only to a slight extent be formed by the light; the greater part of them arise in the body of the emulsion—indeed the size of the crystal nuclei in the different grains must be regulated in accordance with the Maxwell distribution law. There is no doubt that the nuclei contain sulphur compounds in addition to metallic silver. The sole function of the light is to supplement the residue of silver atoms required for the attainment of the necessary size of nucleus. This aspect will be made more clear by the following facts :—

(1) If one exposes a specially sensitive and lightly coated (single grain layer) photographic plate so that—statistically speaking—each grain of silver bromide on the average absorbs one quantum hv of light, one finds (on counting the grains in the developed plate) a just perceptible difference between the exposed and unexposed layers. From this it follows that in fact for each silver bromide grain *one* quantum can make *one* silver atom developable. In this case there is no question of *several* silver atoms

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[1] *J. Chem. Soc.*, **127**, 2764, 1925.

being formed by the light (in the sense of Dr. Frankenburger's question) in the production of a nucleus, because the statistical conditions for this do not exist.   On the other hand, also, all the silver bromide particles will not be rendered developable, but—as we see it—only that fraction in which silver atoms are found in a favourable situation, *i.e.* on the surface of the grain.   Moreover, as a result of his experiments Pohl has arrived at this conclusion independently of us.

(2) On a longer exposure, so that each grain of silver bromide absorbs 10, 100 or even more, quanta *hν*, the number of grains rendered developable does not increase proportionally with the extent of the exposure (as in the case of *X*- or α-rays), but at first more strongly, then less strongly : a fact which must be connected with the different quantities of the nuclei originally present.   It appears further that (by a very strong exposure) even 1000 silver atoms are not necessarily enough to render a grain developable ; in proportion to this grain the original nucleus is, moreover, notably small.

(3) If we treat the plate, before exposure, with oxidation media (*e.g.* with weak chromic acid solution), the sensitivity to light—as distinct from sensitivity to *x*- and α-rays—is substantially decreased, again, because the nuclei originally present are diminished in number and size.

I have dealt with this matter[2] somewhat more in detail because the very natural-seeming question of Dr. Frankenburger has often been asked and because the explanation he has suggested (that the small nuclear proportion of 1 : 300 can be explained by the combined effect of several photolytically formed atoms leading to the production of a nucleus) has already appeared erroneously in the literature.[3]

[2] See further hereon, W. Meidinger, *Z. physik. Chem.*, **144**, 89, 1925.
[3] *E.g.* in R. Lorenz and W. Eitel, *Pyrosole*, p. 218, Leipzig, 1926.

PART IV. PHOTOSYNTHESIS.

INTRODUCTORY ADDRESS.

By Professor E. C. C. Baly.

Delivered on 18th April, 1931.

The following is a short account of an investigation which has been made during the last three years in Liverpool into the problem of photosynthesis.   The work has been carried out by Messrs. C. L. Moore, D. J. Martin, L. B. Morgan and P. F. R. Venables, and myself.

It was shown in previous papers[1] that compounds of the nature of carbohydrates can be synthesised by the action of visible light on a saturated solution of carbonic acid containing in suspension a finely divided powder capable of adsorbing carbonic acid.   The materials used were cobalt and nickel carbonates prepared by the addition of sodium carbonate solution to a solution of cobalt or nickel sulphate, but considerable difficulty was experienced in the removal of the last traces of alkali from the precipitated salts.   It was found to be essential that the preparations be absolutely free

[1] Baly, Davies, Johnson and Shanassy, *Proc. Roy. Soc.*, A **106**, 197, 1927; Baly, Stephen and Hood, *loc. cit.*, p. 212; Baly and Davies, *loc. cit.*, p. 219.

from alkali, since no photosynthesis was observed if any adsorbed alkali was present. It is of some interest to note the fact that the only satisfactory method of testing for the presence of alkali is to pass CO_2 through a suspension of the carbonate in water, and then to evaporate the solution, after filtration, to dryness. The residue must be neutral to B.D.H. universal indicator. After washing, the carbonates were dried at 100° and then heated at 140°-150° for some hours.

Since the washing of the precipitated carbonates was a very tedious process, a new method for the preparation of the nickel carbonate was devised, namely the electrolysis of an aqueous solution of carbonic acid with pure nickel plates as electrodes.[2] The carbonate prepared in this way and dried at 100° and then heated at 140°-150° had only a small photosynthetic activity, but it was found that it became activated by exposure in a finely divided state to white light for 12 to 24 hours.

Nickel and cobalt carbonates, although when active they gave good yields of carbohydrates, possessed certain very definite disadvantages. In the first place their partial solubility in carbonic acid introduced a troublesome factor. In the second place their activity steadily decreased when kept in the dry state, and in the third place their loss of activity under the influence of light was more rapid when in suspension in carbonic acid solution.

In view of the fact that the results described in the earlier communications seemed to prove the fact that the photosynthesis of carbohydrates is a photochemical reaction on a surface, the obvious aim was the preparation of active powders which would be free from the disadvantages of nickel and cobalt carbonates. It is not necessary to give in full detail the results obtained in the search for powders free from every disadvantage, because very many trials led only to disappointment. Some of the observations made during this stage of our work may, however, be recorded, since they are of interest from other points of view than that of photosynthesis.

Having in mind the striking activity of the supported nickel catalysts for the hydrogenation of oils, prepared by Armstrong and Hilditch,[3] in which the nickel is supported on kieselguhr, previously coated with aluminium hydroxide, we investigated the photosynthetic activity of nickel and cobalt carbonates deposited on the same support. It was found that these preparations evidenced no solubility in carbonic acid solution, the difference between the supported and unsupported carbonates being very remarkable. It was also noteworthy that whereas supported nickel and cobalt carbonates showed the characteristic colours of these salts, the catalyst prepared with equimolecular proportions of the two carbonates was almost white, this mixture when unsupported being very dark coloured and almost black when dry. It was found that the photosynthetic activity of the supported nickel carbonate was greater than that of supported cobalt carbonate and mixtures of the two. This was especially true if 1·6 per cent. of thorium nitrate was added to the nickel nitrate before the carbonate was precipitated. The yield of organic matter photosynthesised in two hours at 25° was of the order of 0·0025 gram per gram of the powder. These preparations, however, still had the disadvantage of the difficulty of washing free from alkali. The same is true of preparations of manganese carbonate supported on the same substrate. This catalyst, however, had only a relatively small photosynthetic activity, since the amount of organic matter photosynthesised in two hours was only 0·001 gram per gram of the powder.

[2] Baly and Hood, *Proc. Roy. Soc.*, A **122**, 393, 1929.
[3] Armstrong and Hilditch, *Proc. Roy. Soc.*, A **103**, 586, 1923.

The inherent difficulty of the preparation of these supported carbonates led us to investigate the activity of coloured hydroxides and oxides supported on the same aluminated kieselguhr, and ferric and chromic hydroxides and oxides were selected. Two methods of preparation were adopted. In the first method ammonia was added to a suspension of the aluminated kieselguhr in ferric nitrate, chromium nitrate, or mixtures of the two. In the second method suspensions of the aluminated kieselguhr in solutions of ferric nitrate or ammonium bichromate, or mixtures of the two, were evaporated to dryness and then ignited to form the ferric and chromium oxides. Different amounts of thorium nitrate were also added to the solutions in each of the two methods.

The results obtained were of considerable interest. With the supported hydroxides photosynthetic activity was shown by all the preparations, that is to say by the two hydroxides and their mixtures, the quantity of organic matter photosynthesised being of the order of o·oo2 grams per gram of powder. In the case of the supported oxides prepared by the ignition method organic matter was photo-synthesised by the supported ferric oxide alone. With chromium oxide or mixtures of chromium and ferric oxides, chromic acid was invariably formed, the filtrate after exposure to light being coloured strongly yellow. The same reaction was shown by the supported chromium hydroxide and mixtures of ferric and chromium hydroxides after they had been dehydrated by heating.

It was further observed in the case of the pure supported ferric hydroxide and oxide that the photosynthetic activity varied with the amount of thorium oxide present.

Of the two methods of preparation of the supported ferric oxide catalyst, the second seemed to be far simpler to carry out, since the prolonged washing involved in the precipitation method was avoided. We, therefore, adopted this method with the intention of studying the variation in the photosynthetic activity of the catalyst with the thorium oxide content. The aluminated kieselguhr was prepared in exact accordance with the method described by Armstrong and Hilditch. To a boiling suspension of 100 grams of kieselguhr which had been previously treated with strong nitric acid, in 1000 c.c. of water containing 150 grams of $AlCl_36H_2O$ were added in small portions at a time 100 grams of anhydrous Na_2CO_3, that is to say twice the theoretical quantity. When the whole of the alkali had been added the mixture was boiled for 15 minutes and then filtered. The washing of the product until completely free from alkali was carried out as follows. The product, after as much of the mother liquor as possible had been removed by suction on the filter, was vigorously stirred in two gallons of distilled water, steam being passed in until the whole was boiling. The mixture was then allowed to settle, when the supernatant liquid was syphoned off and the residue filtered. This was repeated many times until the clear filtrate had $f_H = 7$ to 7·5, and in general it was found that this end was not secured until after four days. The aluminated kieselguhr was then heated at 100° until completely dry.

The quantity of Fe_2O_3 to be deposited on this material was calculated on the assumption that one-third of a molecule of Fe_2O_3 was equivalent to one atom of nickel, and since Armstrong and Hilditch found high activity when their catalyst contained 15 per cent. Ni, we adopted 16·67 per cent. Fe_2O_3 calculated on the final product. To obtain this, 40 grams of the aluminated kieselguhr were added to a solution of 40·4 grams of crystallised ferric nitrate and the mixture evaporated to dryness with constant stirring on a sand bath. The dried product was then powdered and heated in a

silica tube in a current of dry CO-free air at 460°. It was then transferred to a second silica tube closed at one end and heated at 400° in a vacuum for one hour in order to remove the adsorbed nitric oxide. Preparations were also made in which the outer layer of ferric oxide contained various amounts of thorium oxide, definite quantities of thorium nitrate being added to the ferric nitrate solution. The results obtained with these powders were most promising. Not only was there found evidence of marked photosynthetic activity, but the yield of photosynthesised products varied periodically with the amount of ThO_2 present.

These results confirmed an opinion formed during the transitional stage of our work that there was some connection between the photosynthetic activity of a powder and the stability of its suspension in carbonic acid solution. Since the stability of a suspension is due to the electric charge on the particles, the sign and magnitude of this charge were determined by the method of cataphoresis. The particles were then found to be electropositively charged and, further, the surface potential was found to be proportional to the yield of photosynthesised products. These facts have been completely established by subsequent work. As the result of numerous experiments, it has been proved that no photosynthesis is obtained with a powder the particles of which carry an electronegative charge. Furthermore, the application of the cataphoresis measurement to preparations of nickel and cobalt carbonates has given an explanation of the difficulties we ourselves met with in employing them as catalysts and the negative results obtained by others in an attempt to reproduce our earlier observations. In repeating the observations with precipitated nickel and cobalt carbonates, it was found that at times the preparations showed a small charge and little activity, the reason apparently being that the washing of the precipitate tends to its deterioration. Small quantities of precipitate and large volumes of water are advisable, the time being reduced as much as possible. On the other hand the electrolytic method of preparation of nickel carbonate is far preferable and gives active powders if the method described in the earlier paper is exactly followed. The cataphoresis measurements with the powder activated by light show how rapid is its deterioration after it is placed in the dark. The zeta-potential of the most active preparations is of the order of + 38 millivolts, and this falls to a very small value within a few hours. When suspended in conductivity water and exposed to white light, the powder loses its activity entirely within two hours, its suspensions in carbonic acid then having a very small charge indeed and no activity. The cataphoresis measurements have proved of the greatest possible service throughout the whole of the more recent work we have carried out.

The promising results given by the powders consisting of ferric and thorium oxides supported on aluminated kieselguhr led us to repeat them in greater detail. A considerable quantity of the aluminated kieselguhr was prepared in accordance with the method already described, and equal portions of this were coated with Fe_2O_3 containing quantities of ThO_2 lying between 2·5 per cent. and 1 per cent. It was then found that sharp maxima of photosynthetic activity occurred at 2·12 per cent. and 1·5 per cent., sharp minima being found on both sides of these maxima. Furthermore, there was found to exist a close proportionality between the photosynthetic activity and the electropositive charge assumed by the powders in saturated carbonic acid solution. At this stage in our work, having used the whole of the supply of kieselguhr in hand, we found ourselves unable to reproduce the results with fresh samples of kieselguhr. Kieselguhr was obtained from different sources, but in each case very disappointing results

were obtained. After many failures it was decided to obtain as large a quantity as possible of a very absorbent kieselguhr and to make a detailed investigation of the whole problem. Our cordial thanks are due to the Nobel Section of Imperial Chemical Industries, Ltd., who very kindly presented us with 84 lbs. of very pure kieselguhr and said that if necessary they would be willing to supply further quantities of similar quality.

The first question to be decided was the best method of coating the kieselguhr with alumina and the optimum quantity to be so deposited. In commencing this detailed work we made the assumption that the optimum to be aimed at during every stage was the maximum possible electropositive charge exhibited by the various preparations when in suspension in water saturated with carbon dioxide. This assumption has been proved to be completely justified.

In the investigation of the right method of deposition of the alumina on the kieselguhr we found in the first place that the method used by Armstrong and Hilditch, namely by precipitation by excess of sodium carbonate, failed in every case to give a satisfactory result, except with the particular sample of kieselguhr used in the experiments already described. Preparations were made containing from 12 to 30 per cent. of Al_2O_3 using aluminium sulphate, chloride and nitrate, but without success. We have not been able to explain the success met with in the first experiments.

The Armstrong and Hilditch method of preparation has the disadvantage of the long time taken in the washing of the product until free from alkali. It seemed advisable to use a method in which the washing could be carried out in the shortest time possible,[4] and the precipitation by the addition of ammonia to a suspension of kieselguhr in aluminium nitrate solution seemed to be the most promising, since it appeared probable that if the product were not completely freed from ammonium nitrate this salt would not interfere with any subsequent process inasmuch as it would be decomposed on heating. It was found, however, that the presence of ammonium nitrate was a serious disadvantage, because the aluminated kieselguhr on drying at 100° became acid in reaction owing to the formation of aluminium nitrate, with the escape of ammonia. It is true that on heating at 450° this aluminium nitrate was converted to the oxide, but the product when in suspension in saturated carbonic acid solution had a reduced surface potential and showed after coating with ferric oxide only small photosynthetic activity.

The coating of kieselguhr with aluminium hydroxide by the addition of ammonia was fully investigated and it was found that, provided the process was carried out in the cold and the product was rapidly washed, the product suffered little deterioration of its surface potential. The effect of prolonged washing and of using hot solutions was a definite decrease in the surface potential.

The next step was the determination of the optimum quantity of alumina to be deposited on the kieselguhr. A number of preparations were made containing different amounts of aluminium hydroxide, and each of these was dried at 100° and then heated at 450° in a silica tube in dry air. Measurements were made of the surface potential in saturated carbonic acid solution and these show that the electronegative kieselguhr loses its charge as small quantities of alumina are adsorbed, until with 1·5 per cent. Al_2O_3 the

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[4] It may be noted that the evaporation to dryness of a suspension of kieselguhr in aluminium nitrate solution, and the ignition of the product until free from nitrate failed to give a satisfactory result. The Al_2O_3 was not adsorbed, a mixture of free oxide and kieselguhr being obtained.

product is electrically neutral. As the quantity of Al_2O_3 is increased the product becomes electropositive and the charge increases to a maximum when the product contains 22 per cent. Al_2O_3. When the quantity of Al_2O_3 is still further increased, the surface potential falls slightly to a value which is apparently constant. This constant value is due to the fact that the kieselguhr is saturated by 22 per cent. Al_2O_3 and when larger quantities of $Al(OH)_3$ are precipitated in the presence of the kieselguhr, mixtures of aluminated kieselguhr and free $Al(OH)_3$ are formed. The cataphoresis measurements obtained after ignition are the mean of those of material containing 22 per cent. Al_2O_3 and of free Al_2O_3, and these naturally have a constant value.

As a result of these determinations it was decided to use aluminated kieselguhr containing 22 per cent. Al_2O_3. It must be remembered that this saturation value refers to the particular sample of kieselguhr presented to us and may depend on the nature of the kieselguhr.

It is necessary that the aluminated kieselguhr be heated in order to convert the $Al(OH)_3$ to Al_2O_3. Our experience has shown that the best method is first to heat the powdered material on a sand bath and then to heat it in a silica tube in a current of dry air at 450°, after which it is coated with Fe_2O_3 or $Fe_2O_3 + ThO_2$.

The method of coating has already been described. It was found that the optimum surface potential was given by powders containing 14 per cent. of Fe_2O_3 or $Fe_2O_3 + ThO_2$. Many series of powders have been prepared containing 0, 0·2, 0·4 . . . 3 per cent. ThO_2 in the Fe_2O_3, the total amount of Fe_2O_3 and ThO_2 being always 14 per cent. of the finished product. The two maxima of the surface potential at 2·1 and 1·5 per cent. of ThO_2 were confirmed and a third maxima was found at 0·72 per cent. Minima were found at 0·38, 1·2 and 1·8 per cent.

Since it is evident that some of the Al_2O_3 tends to dissolve in the ferric nitrate solution during the coating of the aluminated kieselguhr with Fe_2O_3, this will alter the percentage of ThO_2 in the outermost layer. The final determination of the maxima and minima was made by adding known amounts of thorium in the preparation of the aluminated kieselguhr and coating each preparation with Fe_2O_3 containing the same percentage of ThO_2.

It is then obvious that the percentage of ThO_2 in the outer coating will not be altered by the dissolution of any Al_2O_3 in the ferric nitrate solution. The true percentages giving the maxima and minima were determined with the greatest possible care. As an example, the examination of the maximum at about 0·72 per cent. ThO_2 was carried out as follows: preparations of aluminated kieselguhrs were made, containing, respectively, 0·58, 0·60, 0·62, 0·64, 0·66, 0·68 per cent. ThO_2. Each of these was coated with Fe_2O_3 containing, respectively, the same quantity of ThO_2. The measurements of the surface potential showed that the maximum occurred at 0·64 per cent. By similar methods the second and third maxima were found to be at 1·28 and 1·92 per cent., and the minima to be at 0·32, 0·96, 1·60 and 2·24 per cent. In other words, the maxima occur at the even multiples of 0·32 per cent. and the minima at the uneven multiples of 0·32 per cent.

Turning next to the photosynthetic activity of these series of supported ferric oxide catalysts, we have to acknowledge that the investigation is as yet incomplete. Although we have proved that maxima and minima of photosynthesis occur at the maxima and minima of surface potential, the yields have at best been far smaller than our earlier work led us to expect, and at times have been vanishingly small.

In seeking for an explanation of this we have found that the residues obtained after evaporation of the irradiated suspensions in saturated carbonic acid solution have been alkaline. This indicates the presence of adsorbed alkali on the powders and, as has already been stated, this invariably inhibits photosynthesis. We have traced this not to any fault in the preparation of the powders but to the kieselguhr itself, and up to the present time we have not succeeded in removing the source of the trouble. The kieselguhr has been treated in the following ways : it was boiled with nitric acid and washed until free from acid, then heated at 620° and again extracted with nitric acid and washed until free from acid, but extraction with carbonic acid solution still gave an alkaline residue. The kieselguhr was extracted with 7N HCl and washed until free from acid and then heated at 620°, this treatment being repeated three times, and then the extraction with carbonic acid solution appeared to give only a neutral residue. A preparation of a finished powder containing 0·64 per cent. ThO_2 from this treated kieselguhr gave on irradiation of its suspension in carbonic acid solution definite evidence of photosynthesis, but there was much alkali present.

It must, therefore, be confessed that the investigation, although definite conclusions as to the periodic variation of activity have been established, is as yet incomplete and that the limited success is due to the difficulty experienced in the preliminary treatment of the kieselguhr.

THE APPLICATION OF THE PHOTOCHEMICAL EQUIVALENT LAW TO VITAL PROCESSES.

BY PROFESSOR OTTO WARBURG (*Berlin-Dahlem*).

If, in a photochemical process, we measure the absorbed radiant energy Q, we obtain according to the quantum theory the number of absorbing molecules $Q/h\nu$. Setting with Einstein the number of reacting molecules equal to the number of absorbing molecules, we obtain the number of photochemical primary processes.

We will discuss two applications of this principle which are important biologically.

1. Assimilation of Carbon Dioxide.

The thermochemical equation for the assimilation of carbon dioxide in green cells is :—

$$6 CO_2 + 6 H_2O = C_6H_{12}O_6 + 6 O_2 - 674,000 \text{ cal.}$$
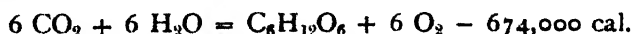
Thus $674,000/6 = 112,000$ calories are required to decompose one molecule of carbon dioxide. The equivalent radiant energy [1] of light of various frequencies amounts :—

> For the wave-length 660$\mu\mu$ to 43,000 cal.
> For the wave-length 578$\mu\mu$ to 49,200 cal.
> For the wave-length 436$\mu\mu$ to 65,100 cal.

[1] This term is used to indicate the energy necessary to decompose one molecule of a substance, assuming the validity of the Einstein photochemical relation.

It is seen that the energy of one quantum is insufficient to decompose one molecule of carbon dioxide; in other words, *several* acts of absorption or *several* elementary processes must co-operate in order to reduce a molecule of carbon dioxide to sugar. Our measurements show that, with red and yellow light four quanta, with blue light five quanta are required to decompose one molecule of carbon dioxide, if in calculating we employ the *total* absorption of the light by the green cells.

With blue light, however, not only the chlorophyll, but also the accompanying yellow pigments of chlorophyll absorb, and it is known that these are photochemically inactive. It is, therefore, more correct to employ in the calculation only the energy absorbed by the chlorophyll. Doing this, we find that with blue light less than 5 and more than 3 quanta, probably 4 quanta, are used in the decomposition of a molecule of carbon dioxide.

The result of the measurement is that the reduction of carbonic acid in green cells takes place by combination of four elementary reactions, or, in other words, in four stages.

The magnitude of the *energy* efficiency in the assimilation of carbon dioxide is obtained by dividing 112,000 cal. by four times the equivalent radiant energy of the light employed. We obtain :—

For the wave-length $660\mu\mu$.   65 per cent.
For the wave-length $578\mu\mu$.   57   ,,   ,,
For the wave-length $436\mu\mu$.   43   ,,   ,,

2. Chemical Constitution of the Respiratory Ferment.

Mond and Langer found in 1891 that iron pentacarbonyl gave off carbon monoxide on exposure to light. Subsequently it has been shown that in this case we have a very general property of the iron carbonyl compounds : all such compounds so far tested dissociate on illumination.

We have studied this reaction quantitatively and found that, in general, for the visible region of the spectrum one molecule of carbon monoxide results for each light quantum absorbed.

Consider now an iron carbonyl compound, whose coefficient of light absorption is for some reason not directly measurable. A very thin layer of this iron carbonyl compound is exposed to light of different wave-lengths and of known intensities, it being possible to determine the carbon monoxide split off. If for two wave-lengths, 1 and 2, the photochemical effects are w_1 and w_2, the incident "quantum intensities" i_1 and i_2, the coefficients of light absorption β_1 and β_2, then, since Einstein's law holds, the photochemical effects are proportional to the absorbed quanta

$$\frac{w_1}{w_2} = \frac{\beta_1 i_1}{\beta_2 i_2} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

According to this equation we can determine the *relative* absorption spectrum of an iron carbonyl compound by measuring the photochemical effect w and the incident "quantum intensity" i. Further, consider again a very thin layer of an iron carbonyl compound exposed to light of the "quantum intensity" i. This time we follow the course—from time to time—of the liberation of carbon monoxide and calculate therefrom the velocity constant z of the photochemical decomposition for the light intensity i.

$$z = \frac{-dn}{dt} \Big/ n \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where n is the number of $Fe(CO)_5$ molecules in the illuminated layer.

Since the Einstein Law holds, the number of the molecules decomposing per minute is equal to the number of quanta absorbed per minute

$$\frac{-dn}{dt} = i \,.\, \beta \,.\, dx \,.\, q \,.\, c \qquad . \qquad . \qquad . \qquad . \quad (3)$$

where i is the incident "quantum intensity," β the coefficient of light absorption, dx the thickness of the layer, q the cross-section of the illuminated layer, and c the concentration of the iron carbonyl compound.

The number of molecules present in the illuminated layer is

$$n = dx \,.\, q \,.\, c \qquad . \qquad . \qquad . \qquad . \quad (4)$$

Dividing (3) by (4) and bearing (2) in mind, we obtain

$$z = i \,.\, \beta \qquad . \qquad . \qquad . \qquad . \quad (5)$$

This equation can be employed to calculate the absolute value of the absorption coefficient (presumed to be unknown) of the iron carbonyl compound.

Application to a Vital Process.—The respiration of living cells is retarded if carbon monoxide be added to the air in which the cells are respiring. If the cells containing carbon monoxide be illuminated, they begin again to respire, and thus by alternate illumination and darkening one may bring about alternate non-respiration and respiration.

Respiration stops in the dark because the carbon monoxide reacts with the catalyst for the respiratory process and protects it from oxygen. Respiration reappears on illumination because the compound between the catalyst and carbon monoxide dissociates. The catalyst for respiration thus behaves like an iron carbonyl compound, exhibiting the Mond reaction.

Fig. 1.—Absolute absorption spectrum of the carbonic oxide compound of the respiration ferment. Dimension of the absorption coefficients [sq. cm./gram-atoms Fe].

Admittedly one cannot now directly measure the light reaction, because the concentration of the catalyst is too small. But one can calculate from the velocity of the catalysed process—here, the respiration—what fraction of the catalyst is combined with carbon monoxide and what fraction is free.

If a thin cell layer in carbon monoxide be illuminated with light of varying wave-lengths and the resulting respiration measured, the case of equation (1) applies and the *relative* absorption spectrum of the carbon monoxide compound with the catalyst may be calculated. If the cell layer previously left in the dark be illuminated and then measurements be made of the increase in velocity of respiration in going from retardation to non-retardation, the photochemical decomposition constant (2) of the iron carbonyl compound is obtained and from equation (5) the absolute absorption coefficient of the carbon monoxide compound of the catalyst may be calculated.

In Fig. 1 the so-obtained absolute absorption spectrum of the carbon monoxide compound of the catalyst is graphically depicted. The spectrum here shown is the spectrum of a carbon monoxide hæmin.

PHOTOSYNTHESIS IN TROPICAL SUNLIGHT.

By N. R. Dhar, Gopala Rao, and Atma Ram.

Under the action of sunlight, the green plants absorb carbon dioxide from the air and transform it with the intervention of water into carbohydrates. This phenomenon has been technically called photosynthesis or carbon assimilation. The reaction,

$$nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2,$$
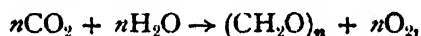
is endothermic and the quantity of energy absorbed is approximately 110,000 gr. calories for each gram molecule of carbon dioxide. The green plant is thus an efficient converter of the inexhaustible supply of solar energy into potential energy in the shape of food materials, fuel, etc. Coal and petroleum are likewise the product of photosynthetic activity produced ages ago. Thus it becomes evident that all life on this planet, our gigantic industrial developments of the modern era depend on this phenomenon of photosynthesis, which in the ultimate analysis becomes the prime mover of life and civilisation.

Despite numerous researches, the mechanism of photosynthesis is not yet clear. During recent years Baly and co-workers,[1] Dhar and collaborators,[2] and Mezzadroli and co-workers[3] have done much to elucidate the mechanism of the reaction by experiments *in vitro*. In this communication we are giving a brief survey of our work on (1) Photosynthesis of formaldehyde, (2) polymerisation of formaldehyde to reducing sugars, and (3) photosynthesis of nitrogenous compounds.

Photosynthesis of Formaldehyde.

Carbon dioxide was passed through aqueous suspensions of various photocatalysts exposed to sunlight and contained in glass vessels. In view

[1] *J. Chem. Soc.*, 119, 1025, 1921 ; *Proc. Roy. Soc.*, 116, 197, 1927 *et seq.* ; *Nature*, October 25, 1930.
[2] Dhar and Sanyal, *J. Physical Chem.*, 29, 926, 1925 ; Gopal Rao and Dhar, *J. Physical Chem.*, 35, 1931.
[3] *Atti R. Acad. Lincei*, 6 (vi), 160, 1927 ; *ibid.*, 8, (iv), 511, 1928 ; *Gazetta*, 59, 305, 1929.

of the criticism of Porter and Ramsberger,[4] who attribute the origin of formaldehyde formed to the impurities present, such as stopcock grease, rubber tubing, sealing wax, etc., we had recourse to the following method of proving the non-interference of impurities. The gas was passed through a two-way tube simultaneously into two beakers, one containing the reaction mixture and the other conductivity water. After three hours' exposure to sunlight both the solutions (the first one after distillation) were tested for formaldehyde. In every case formaldehyde was detected in the reaction mixture, and not in the blank. The test utilised was Schryver's reagent. The yield of formaldehyde varied from 20 to 50 times the sensitiveness of the test ; so that the results could not be attributed to experimental error.

(a) *From Inorganic Coloured Substances and Sunlight.*—Carbon dioxide was passed through aqueous solutions or suspensions of the following substances : (1) cobalt carbonate, (2) nickel carbonate, (3) copper acetate, (4) manganous chloride, (5) uranium nitrate, (6) ferrous sulphate, and (7) ferric chloride. In the case of the first five substances only formaldehyde was formed, no reducing sugar being detected. While with ferrous sulphate, no formaldehyde but glucose only was obtained. In the case of ferric chloride, both glucose and formaldehyde were formed. The yield of formaldehyde was slightly higher with silica vessels than with glass ones. Other photocatalysts like colloidal ferric hydroxide, copper carbonate, copper sulphate, chromium oxide, chromium sulphate, etc., gave lesser yields than the above substances.

In order to obtain a higher concentration of carbon dioxide, it was thought advisable to use solutions of sodium bicarbonate. Two per cent. solutions of sodium bicarbonate were sealed up with photocatalysts and exposed to sunlight, blank experiments being set up side by side. The results are as follows :—

2 per cent. solutions of sodium bicarbonate with cobalt carbonate	Only formaldehyde.
2 per cent. solutions of sodium bicarbonate with nickel carbonate	Appreciable quantities of formaldehyde and glucose.
Carbon dioxide (saturated solution of) and ferric hydroxide sol	Formaldehyde and carbohydrate.
2 per cent. solution of sodium bicarbonate and copper bicarbonate . . .	Only formaldehyde.

Temperature coefficient of formaldehyde formation was found to be 1·5.

(b) *From Organic Dyestuffs and Sunlight.*—Chlorophyll, methylene blue, malachite green, and methyl orange were used with success. In this case, a complication is introduced because the dyestuffs themselves decomposed in aqueous solution on exposure to sunlight with the formation of small quantities of formaldehyde.[5] Therefore, we always exposed a blank solution of the dye under exactly identical conditions, except that no carbon dioxide was passed through it. The blank solution and the solution through which carbon dioxide was passed were distilled and the distillates tested for formaldehyde with Schryver's reagent. Comparative experiments showed that in every case in which carbon dioxide was passed, considerably larger quantities of formaldehyde were produced than in the absence of carbon dioxide. These experiments repeated several times leave no doubt

[4] *J. Amer. Chem. Soc.*, **47**, 79, 1925.
[5] *Cf.* Baur and Rebmann, *Helv. Chim. Acta*, **5**, 828, 1922, and Baur and Buchi, *ibid.*, **6**, 959, 1923 ; Osterhout, *Amer. J. Botany*, **5**, 511, 1918.

that carbon dioxide is reduced to formaldehyde, in the presence of light and such dyestuffs.

It appears that, during the course of photosynthesis some of the dyestuff was oxidised; because the colour of the solution through which carbon dioxide was passed was found to be less intense than that through which no carbon dioxide was passed, but was nevertheless exposed. We believe that chlorophyll besides being an optical sensitiser also takes a chemical part in photosynthesis.

The Reduction of Carbon Dioxide to Carbon Monoxide.—When carbon dioxide was passed through chlorophyll suspension exposed to visible light, we detected traces of carbon monoxide in the issuing gases. The bearing of this on the photosynthesis mechanism will be discussed later.

Formaldehyde from Nascent Carbon Dioxide.—A suspension of barium carbonate was exposed in a flask to sunlight; and dilute hydrochloric acid was allowed to drop into the flask from a burette at a very slow rate; when the incoming drop of hydrochloric acid came in contact with the barium carbonate some carbon dioxide was evolved. It was found that considerable quantities of formaldehyde amounting to 0·002 per cent. of the solution were formed. Similar results were obtained with calcium and strontium carbonates. Blank experiments were always performed.

The Polymerisation of Formaldehyde to Reducing Sugars.

Three per cent. solutions of formaldehyde were exposed to sunlight with various photocatalysts, both in open vessels and in closed bulbs, for periods varying between 30 to 60 hours. Ferric chloride, chlorophyll, and nickel carbonate are good polymerising agents photochemically. Part of the ferric chloride was reduced to ferrous salt which appeared to retard the polymerisation. In testing for sugars, of course, all the inorganic salts were removed. The sugars obtained reduced Benedict's solution, gave the Molisch and Rubner reactions.

As the yield with ferric chloride appeared to be good, it was thought profitable to determine the temperature coefficient of this polymerisation. 800 c.c. of 3 per cent. formaldehyde solution were exposed in a sealed bulb with sufficient ferric chloride for 45 hours at 30° and 40°. At 30° the amount of reducing sugar formed corresponded to 0·061 g. of copper oxide, while that at 40° to 0·077 g. Therefore, the temperature coefficient is

equal to $\dfrac{·077}{·061} = 1·26$.

Nitrogenous Compounds.

The only experiments that yielded good results are the following :—

2 per cent. HCHO + Ammonia + Titanium dioxide: examined after 30 hours; found hexamethylene tetrammine, urethane and little nitrite.

2 per cent. HCHO + Ammonia + Titanium dioxide: examined after 60 hours; found hexamethylene tetrammine, no urethane but an oily basic substance.

2 per cent. HCHO + Ammonia + Copper carbonate: examined after 16 hours found hexamethylene tetrammine and methyl amine (hydrochloride M.P. 95·9°).

Discussion of Results.

We obtained considerable quantities of formaldehyde when carbon dioxide was passed into aqueous suspensions of nickel carbonate, cobalt

carbonate and other photocatalysts in presence of tropical sunlight. Reducing sugars were obtained only in a few cases, while formaldehyde was detected in all the cases, including the above. Baly and co-workers obtained reducing sugars only and no formaldehyde under similar circumstances. The cause of this discrepancy is not yet clear, except that the intensity of light in our experiments is greater than theirs, our experiments having been carried out in tropical sunlight.

We believe that formaldehyde is an essential intermediate stage in the formation of sugars. From our experiments on the photochemical decomposition of carbon dioxide to carbon monoxide, we are of opinion that such photocatalysts as chlorophyll play an essentially chemical rôle, besides absorbing the radiant energy. We have observed that chlorophyll and other dyestuffs are appreciably oxidised after vigorous photosynthesis. We postulate that chlorophyll and carbonic acid interact with the formation of a peroxide type of compound, and the liberation of nascent carbon monoxide. This in its turn interacts with water to give formaldehyde and oxygen. The chlorophyll peroxide slowly decomposes thermally with the liberation of oxygen and the formation of chlorophyll. These reactions are symbolised by

$$\text{Chlorophyll} + H_2CO_3 = \text{Chlorophyll peroxide} + \underset{\text{nascent}}{(CO)} \qquad . \quad (1)$$

$$\underset{\text{nascent}}{(CO)} + H_2O = H.CHO + (O) \quad . \qquad . \qquad . \quad (2)$$

$$\text{Chlorophyll peroxide} = \text{Chlorophyll} + (O) \qquad . \qquad . \quad (3)$$

$$n\text{HCHO} = (H.CHO)_n \text{ (Carbohydrate)}.$$
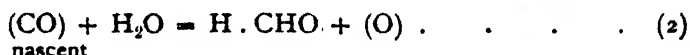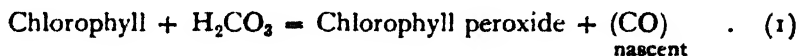
The oxidation of chlorophyll and its slow regeneration from the oxidised product are supported by the fatigue experiments of Pantanelli and Ursprung. Further evidence in favour of our view is obtained from the experiments of J. Wlodek [6] on the variation of the ratio of chlorophyll-*a* to chlorophyll-*b* in the leaves of potato, sugar beet, and *Iris germanica*. It is interesting to note that during the day, that is, when photosynthesis is taking place, the ratio falls corresponding to an increase in chlorophyll-*b*, which is richer in oxygen than chlorophyll-*a*. At night, the porportion of chlorophyll-*b* falls while that of chlorophyll-*a* rises. Similar oxidation of the photocatalyst appears to have been noticed by Baly and co-workers working with nickel and cobalt carbonates: with nickel carbonate the surface is coated with black Ni_2O_3. It appears, therefore, certain that photocatalysts whether *in vitro or vivo* serve in a dual capacity: (1) they absorb the radiant energy necessary for photosynthesis, and (2) they act by virtue of their reducing action.

The chemical rôle of chlorophyll is also supported by the researches of Warburg on the effect of carbon dioxide concentration on the rate of photosynthesis. With increasing carbon dioxide concentration above a certain amount, Warburg found that the increase in the rate of photosynthesis rapidly falls off until a certain concentration of carbon dioxide, further increase in the latter produces no effect. It is clear that the rate of photosynthesis depends not only on the concentration of carbon dioxide, but on that of some other substance as well, with which carbon dioxide reacts. According to our hypothesis, carbon dioxide interacts with chlorophyll. At low concentrations of carbon dioxide when the chlorophyll content is comparatively in excess, it is clear that photosynthesis will increase with

[6] *Bull. Acad. polonaise Sci. l.*, *Sci. Math. Nat.*, B 19, 1920; B 143, 1921.

increasing concentration of carbon dioxide. But this will not proeeed *ad infinitum.* The content of chlorophyll being limited, a certain stage will be reached when increase in carbon dioxide concentration produces no further increase in the rate of photosynthesis.

According to our scheme the evolution of oxygen takes place in two stages (2 and 3). That this is so is shown by the experiments of Kostyschew [7] and confirmed by Spoehr and McGee,[8] who found that the ratio of carbon dioxide to oxygen, during illumination, varies with time. They found that during photosynthesis the leaves absorb initially more carbon dioxide than oxygen is given off. After a short time these conditions are reversed and finally the ratio attains the constant value of 1. If, in the above scheme, the two reactions (2) and (3) proceed at different rates, then the above results of Kostyschew, Spoehr and McGee are explicable, as the oxygen is evolved in the two stages (2) and (3). That there are two stages in photosynthesis, a photochemical and a thermal one, is also indicated by the researches of Blackman and Miss Mathaei,[9] and Warburg on the relation of light intensity and temperature coefficient; for details, compare Gopala Rao and Dhar.[2]

The present hypothesis thus accounts for most of the facts of photosynthesis in *vivo and vitro.*

Summary.

1. Formaldehyde has been obtained from carbon dioxide and water in the presence of various organic and inorganic photocatalysts and sunlight. Traces of glucose have also been found in a few cases.

2. Polymerisation of formaldehyde to reducing sugars have been effected in the presence of photocatalysts like ferric chloride, nickel carbonate and chlorophyll.

3. Few cases of synthesis of complex nitrogenous compounds are also reported.

4. A new hypothesis for explaining the mechanism of photosynthesis has been put forward.

[7] *Ber. bot. Ges.,* **39**, 319, 1921.   [8] *Amer. J. Bot.,* **11**, 493, 1924.
[9] *Phil. Trans.,* **197**, 47, 1905.

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GENERAL DISCUSSION.

Mr. C. F. Goodeve and Dr. J. Bell (*communicated*) : It is difficult to understand the sharpness of the maxima and minima of cataphoretic activity obtained by Professor Baly and the exact meaning of "percentage composition" of such a complex heterogeneous catalyst. In the method of preparation used, evaporation would produce crystals of ferric and thorium nitrates which on ignition would produce a catalyst of widely varying composition. As mentioned in footnote 4, the preparation of aluminated kieselguhr by a similar method produces merely a mixture of alumina and kieselguhr. We have prepared catalysts in a manner identical to that described by Professor Baly and on analysis have found variations in the iron content with particle size amounting to five to ten per cent. of the iron content. It would seem that the variation in the thorium oxide content of particles must be at least as large as this.

Professor J. Eggert (*Leipzig*) asked whether irradiation by light of definite wavelength, by reference to the adsorption bands of the supporting substance (*e.g.* red in the case of $NiCO_3$ etc.) had been tried.

Professor O. Warburg (*Berlin*) asked whether a simpler and safer method would not consist in measuring manometrically the amount of carbon dioxide which is destroyed under the influence of light, instead of determining the reduction products by chemical means. If it happens that in an apparent photosynthesis *no* oxygen is evolved, there would be a negative pressure of the carbon-dioxide in the gas space. *If, however, oxygen is formed,* a positive pressure will appear if the experiment is so conducted that the volume of liquid in the reaction vessel is large relatively to that of the gas space. Having regard to the relative solubilities of carbon-dioxide and oxygen, it follows that the positive pressure due to the evolution of oxygen is greater than the negative pressure due to the destruction of carbon-dioxide. If we know the respective volumes of the gas and liquid spaces we can readily calculate the amount of carbon-dioxide photochemically decomposed, in the first place from the negative pressure, and in the second from the positive pressure.

The **President** said : With reference to Professor Baly's observation as to the sudden cessation of the activity of Ni and Co carbonates in the presence of excess of alkali and the difficulty of neutralisation, I may draw attention to my similar experience when studying the optimum conditions for obtaining colloidal subcarbonate of copper, and of the importance of avoiding any excess alkali as described in a paper published by myself and Dr. Heberlein in the *Transactions of the Chemical Society* in 1917 or 1918.

Dr. F. A. Freeth (*London*) said : Has Professor Baly considered using an amorphous substance like condensed acetylene. I find it difficult to imagine a more variable substance than kieselguhr.

Professor F. G. Donnan (*London*) said : Professor Baly has stated that part of the energy required in the assimilation process is derived from the solid adsorbent. I should like to know the theoretical basis for this view, *i.e.*, a precise statement of the energy-relationships concerned in the process.

Dr. W. Frankenburger (*Ludwigshafen*) said : The following process may serve to explain how far the energy requirements of the assimilation process during adsorption of the reagents on the catalyst or sensitiser can be calculated in terms of the value Q for gaseous reaction components :—

$$
\begin{array}{ccc}
\underset{\text{(gaseous)}}{H_2O + CO_2} & \xrightarrow{\quad -Q \quad} & \underset{\text{(gaseous)}}{H_2CO + O_2} \\[2mm]
+A \Big\downarrow & & \Big\uparrow -D \\[2mm]
\underset{\text{(adsorbed)}}{H_2O + CO_2} & \xrightarrow{\quad -Q' \quad} & \underset{\text{(adsorbed)}}{H_2CO + O_2}
\end{array}
$$
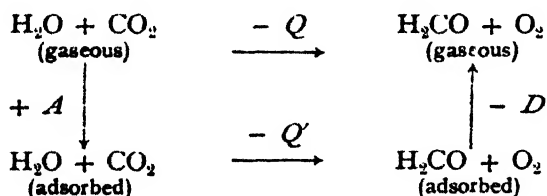
From this scheme we see that the energy requirements of the assimilation process on the adsorbent (Q') will be decreased by the difference ($D - A$) between the heat of adsorption of the *end-products* and that of the reagents over Q. It appears to me that there are principally two cases :—

(1) If the assimilation process takes place in *one* photochemical act, H_2CO, or a carbohydrate, with O_2 is formed. It is unlikely that this will be bound with a much greater energy to the adsorbent than the starting

materials H_2O and CO_2; in this case, also $(D - A)$ is small and Q' can be only slightly different from Q.

(2) The assimilation process takes place by different photochemical step reactions through intermediate products. It is in this case quite conceivable that intermediate products exist (e.g. peroxides, etc.) which are notably more strongly held on the adsorbent than are the starting products; that is to say, in this case we should have $D > A$ and $Q' < Q$. The consequence of this would, however, be that these intermediate products would be bound fast on the adsorbent, and it is conceivable that only by a further photochemical process these intermediate products would be converted into the end products. This accords, moreover, with the quantum measurements of Warburg.

Put shortly, in my view the conception of the adsorption involving a reduction of the energy requirements corresponding to the empirically required $h\nu$ by no means suffices to explain the assimilation, if this takes place in one primary act; on the other hand it can readily be understood if the act of assimilation takes place in several distinct photochemical processes, i.e. if it takes place by means of an intermediate formation of compounds between the adsorbent and the bodies taking part in the reaction.

Professor E. C. C. Baly said, in reply to Mr. Goodeve and Dr. Bell, it may be pointed out that the effect of the thorium oxide content has been found to vary with the nature of the catalyst. In the photosynthetically active preparations of supported ferric oxide the maxima and minima were very sharp and the differences in the activities at these points were very great. In the case of the recent preparations which were photosynthetically inactive the maxima and minima of surface potential were much less well defined and, furthermore, the differences between the surface potentials at the maxima and minima were considerably smaller. We have no explanation of this difference between active and inactive preparations, but the experimental evidence so far as it goes is in agreement with the analytical observations of Mr. Goodeve and Dr. Bell with inactive preparations.

In reply to Professor Eggert, I may say that a few observations were made on the effect of different wave-lengths of light on suspensions of nickel carbonate. It was found that red light of about 7000 Ångströms was the most effective. Definite evidence of photosynthesis was also obtained by irradiation of the suspension with the rays transmitted by a thin screen of biotite.

The energy relationship is undoubtedly a matter of the greatest interest and importance, but we have not as yet made any quantitative determinations of the quantum efficiency of the process, because it has seemed to us that our first aim should be the preparation of active powders by a standardised method which could be reproduced without difficulty. Mention may, however, be made of some observations made on the effect of varying the intensity of the light on suspensions of the ferric oxide powders. These indicated that the yield of photosynthesised material was approximately constant even though the intensity of the light was varied in the ratio of 4 to 1. Furthermore, it seems only possible with a given weight of an active powder to obtain a definite quantity of photosynthesised material. This latter fact has been attributed to the poisoning of the powders by oxygen, the adsorbed layer of oxygen being assumed to be very difficult to displace by carbonic acid.

Both these observations may, however, have a different explanation,

namely that the photosynthetic process is non-catalytic. It is possible that there are present in the surface of the powders a number of active spots, this number varying with the thorium oxide content, and that these spots are capable of activating the carbonic acid to such an energy level that on exposure to red light a quantum efficiency of 1 is observed. This could only be secured if the amount of energy supplied by the active spots to the carbonic acid is of the order of 80,000 to 90,000 calories per gram molecule. It is, however, known to be possible to stimulate reactions involving such large energy increments by means of a surface which thereby undergoes a definite change in physical state.

It may be pointed out that this suggestion also offers an explanation of the activity of nickel carbonate, which is only activated by irradiation when in the dry state. This active state rapidly deteriorates in the dark, it being necessary to use the carbonate immediately after activation. It may be concluded that in this case the photosynthetic process cannot be one of catalysis since it seems to depend on a supply of energy given to the powder by irradiation and to come to an end when this added energy has been utilised.

THE MEASUREMENT OF ULTRAVIOLET RADIATION, ESPECIALLY OF THE PHYSIOLOGICALLY ACTIVE ULTRAVIOLET (WHICH PRODUCES ERYTHEMA), BY MEANS OF THE PHOTOCHEMICAL FORMATION OF TRIPHENYLMETHANE DYESTUFFS FROM THE LEUCO COMPOUNDS.

By Edith Weyde and W. Frankenburger.

(*Communication from the Oppau Research Laboratory of the I.G. Farbenindustrie Aktiengesellschaft Ludwigshafen a. Rh.*)

It is known from the work of Lifschitz [1] that the colourless alcoholic solutions of the *leuco cyanides of the triphenylmethane dyestuffs* or the aqueous *leuco sulphite solutions* become very strongly coloured on irradiation with ultraviolet light (formation of the corresponding dyestuff). These colour changes can be reversed in the dark on addition of potassium cyanide and sulphurous acid respectively.

We investigated this photochemical change of the leuco compounds of *crystal violet* with the intention of working out a method of measuring ultraviolet light. There are two ways of applying this reaction : using *pure leuco cyanide* (sulphite cannot be used in this case) or, *the solutions of leuco compounds with the corresponding additions, which reverse the colour change.*

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[1] Lifschitz, *Ber.*, **52**, 1419, 1919 ; **61**, 1463, 1928 ; *Z. physik. Chem.*, **97**, 426, 1921.

The *pure leuco cyanide solutions* are suitable for a laboratory method, as the following results show ; the coloration on illumination is proportional to the light intensity up to a certain degree of colour change. For monochromatic light the absolute value of the energy of the radiation may be determined from the number of dyestuff molecules formed, since the quantum efficiency $= 1$. The colour change due to illumination was compared colorimetrically (visually) with an alcoholic solution of crystal violet of known concentration.[2] As comparatively small amounts of crystal violet can easily be measured, this method is extremely good for determining very small intensities of radiation,[3] especially if one uses the device of illuminating the leuco cyanide solutions in thin layers with large surface area and using thick layers for the colorimetric comparison.

The *leuco compounds with addition of a substance which reverses the colour change* have the advantage that a great number of measurements can be carried out with the same amount of solution, and therefore make it possible to construct a simple instrument for the measurement of the therapeutically active U.V., which indeed plays an important rôle in medicine to-day.

The working out of both methods required that the photochemical reaction should be investigated at least so far as was necessary to give a sufficiently accurate picture of its course ; further, it was necessary to know the absorption and active spectra of the solutions used. By the active spectrum we mean the spectral dependence of the photochemical dye formation ; absorption and active spectra are identical only when the chemical efficiency of the radiation is equal for all absorbed wavelengths. This question makes necessary the determination of the quantum efficiency, which also is of more general interest, since comparatively simple relationships are to be expected for this ·intermolecular change.[4]

There are a number of further conditions for the development of an instrument for practical purposes, *e.g.*, the active spectrum of the solution used must agree with the spectrum of the sensitivity of the skin, and also the reaction must be independent of temperature within the limits occurring in practice.

Our investigations are only reported here in so far as they are of interest for the methods of measurement ; some further results and details, especially on the course of the reaction, will be published elsewhere.

I. The Change of the Leuco Cyanide of Crystal Violet.

According to Lifschitz,[5] on illumination of an alcoholic leuco cyanide solution the nitrile changes into the cyanide of the dye, which further dissociates into its ions. If one denotes the crystal violet radicle by KV, then :

$$(KV \cdot NC) \underset{dark}{\overset{light}{\rightleftharpoons}} (KV) \cdot CN \underset{dark}{\rightleftharpoons} (KV) + CN^-.$$
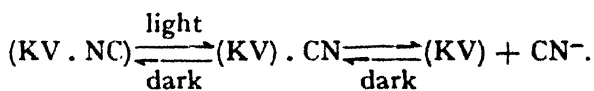
" nitrile," colourless $\longrightarrow$ " cyanide," coloured.

[2] More accurate and objective measurement is possible with photoelectric cells.
[3] E. Weyde, W. Frankenburger, and W. Zimmermann, *Naturwiss.*, **18,** 206, 1930.
[4] See also Lifschitz, *Z. wiss. Phot.*, **29,** 91, 1930.
[5] Lifschitz, *Z. physik. Chem.*, **97,** 426, 1921.

This reaction is reversible ; the colour change goes back again very slowly, correspondingly faster on addition of potassium cyanide.

(a) **The Photochemical Transition of the Nitrile.**—Fig. 1 shows the course of the photochemical formation of the dye for two different concentrations of leuco cyanide. One sees that the formation of dyestuff for a given light intensity is proportional to the time of illumination until a certain amount is converted, then the reaction slows down, due, on the one hand, to absorption by the dyestuff formed, and on the other, to decrease in concentration of leuco cyanide. Also the dyestuff formation is only proportional to the intensity of illumination up to a certain degree of change (for particulars, see spectroscopic part). The change of the nitrile into cyanide is quantitative within the accuracy

Time of irradiation (minutes).
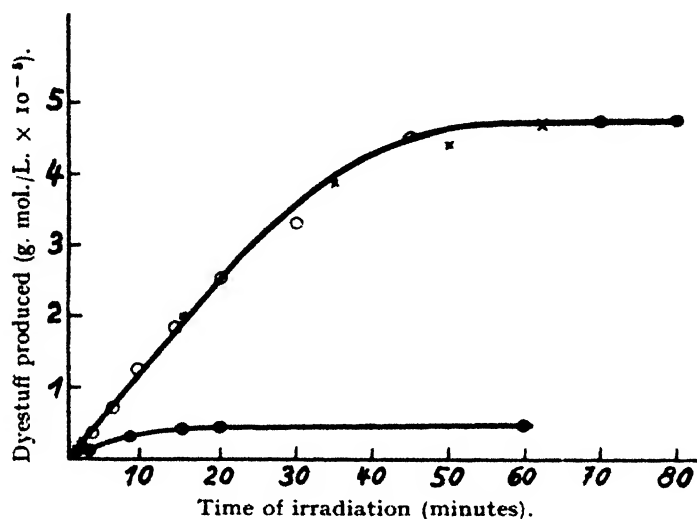
FIG. 1.

o Experiment 1 $4·75 \times 10^{-5}$, g. mol./L. $\times 10^{-5}$ Leuco cyanide.
×   ,,   2   ,,   ,,   ,,   ,,   ,,
⊗   ,,   3 $0·47$,,   ,,   ,,   ,,   ,,

of the measurements. Within the experimental error (variations of the source of light) the light reaction is independent of temperature between $-6°$ and $+40°$.

(b) **The Reverse Dark Reaction.**—Qualitatively one can say that the velocity increases with the amount of potassium cyanide added. However the relationship is not quite so simple, since water (especially the first traces) checks the reaction extremely strongly, apparently in consequence of the hydrolysis of the potassium cyanide ; only the 'CN-ions seem to be effective for the reverse reaction. To obtain measurable reaction velocities (visible decolorisation in a few minutes), the concentration of the cyanide must be distinctly higher than that of the leuco-cyanide. The velocity of the reaction, for given quantities of potassium cyanide and water, is proportional to the number of dyestuff molecules still present. The influence of water also is observed in the very slow decolorisation of the photochemically coloured solutions containing no additional KCN. When using as absolute alcohol as possible (99 per cent.) some decolorisation is already observed within one day ; solutions

containing 5-10 per cent. water, however, show no measurable change, even after two months. The dark reaction is very dependent on temperature, its velocity increasing to about fivefold for 10 degrees rise in temperature.

(c) **The Photochemical Change of the Leuco Cyanide Solution Containing KCN.**—If one illuminates leuco cyanide solutions containing KCN a stationary colour, depending on the intensity of illumination and the temperature, is soon produced. The stationary state is reached, at a given temperature, when the velocity of the dyestuff-forming photochemical reaction is equal to that of the dye-removing dark reaction.

One can illuminate leuco cyanide solutions containing no additional KCN for a long time (up to thirty-six hours at least) without measurable destruction by photochemical side reactions of the maximum coloration obtained. The dyestuff formed will not be changed further photochemically. In solutions containing KCN, however, complete destruction of the leuco cyanide occurs on long illumination, the solution becoming distinctly yellow. This destruction is the quicker the more nitrile is present, owing to the reverse dark reaction. It seems, therefore, as if the nitrile is influenced photochemically in a second way too. Consequently, the destruction of the leuco-cyanide by illumination of the solutions containing KCN takes place in a manner similar to autocatalysis, since the disappearance of nitrile increases the relative concentration of KCN so as to favour the dark reaction and hence the destruction.

(d) **Experimental Method of the Above Investigations.**—A Heræus quartz mercury lamp (DC) was used as source of light (thus not monochromatic light). A glass tube, closed at the bottom end with a quartz plate, served as a reaction vessel. The contents could be stirred by nitrogen, which after drying first was led through a bottle containing absolute alcohol at the same temperature as the reaction vessel, as otherwise the high vapour pressure of alcohol would cause a decrease in the volume of the reaction solution. The reaction vessel could be placed in a cooler which could be regulated at different temperatures. The colour change produced by the illumination was determined visually with a Leitz colorimeter (setting to equal colour strength, changing the thickness of the layer by immersing massive glass rods). The dimensions of the reaction vessel were so arranged that it could be used at the same time as a measuring vessel.

The leuco cyanide was prepared according to the well-known method,[a] recrystallised five times from benzene and dried in vacuum over paraffin oil. For comparison an alcoholic solution of crystal violet of known concentration was used. For this purpose, the crystal violet was recrystallised several times from alcohol and water ; repeated precipitation with ether of the dyestuff from its alcoholic solution also proved useful. In some cases the solution of leuco cyanide was made up from a weighed amount of substance. Owing to the small solubility of this substance it is, however, advisable to use saturated solutions ; 1 litre alcohol dissolves at room temperature $5 \cdot 8 \times 10^{-5}$ gram mol. $= 0 \cdot 023$ g. leuco cyanide. It should be noticed that for the production of a saturated solution the leuco cyanide takes a long time to dissolve.

[a] For its purification, see also Lifschitz, *Z. physik. Chem.*, **97**, 426, 1921.

II. The Conversion of the Leuco Sulphite of Crystal Violet.

The leuco sulphite solution is prepared most easily by leading SO_2 into an aqueous solution of crystal violet. The larger the excess of SO_2, the more the reverse dark reaction will be favoured. Contrary to the case of the leuco cyanide solution, it is impossible to prepare colourless leuco sulphite solutions containing no excess SO_2, such solutions being always coloured at room temperature. Otherwise the leuco sulphite solution behaves (at least qualitatively) just in the same way as the leuco cyanide solution. In the case of leuco sulphite the reaction mechanism is less clear than in that of the leuco cyanide. The investigations are much more difficult to carry out, because one has, for example, to work in a closed vessel in order not to lose SO_2 or have the solutions changed by oxygen (oxidation of the sulphurous acid). Consequently our researches on this substance were restricted to testing whether it could be used in an apparatus for measuring ultraviolet radiation. For this special case the leuco sulphite solutions have considerable advantages over the leuco cyanide solutions, e.g., it is possible to make more concentrated solutions of them, so that the photochemical destruction of the initial substance, which takes place for leuco sulphites in the same way as for leuco cyanides, then will be of relatively less importance. Above all, it is possible to prepare solutions of which the photochemical colour change between about 10-30° C. is independent of temperature. This results from a superposition of different reactions with temperature coefficients of opposite sign, e.g., the solubility of SO_2, the formation of $'HSO_3$ and $''SO_3$ ions.

III. Spectroscopic Part.

The spectrum was recorded by Henri's method. A hydrogen lamp (Geisler tube) working at 8000 volts, which emits a continuous spectrum in the ultraviolet, served as a source of light. A Zeiss quartz spectrograph was used. The measurements of alcoholic crystal violet and leuco cyanide solutions (the latter illuminated previously until the coloration was maximum) and of the decomposition product were carried out in the usual way. The colourless leuco cyanide solution (nitrile) could not be measured in the same simple way, because it changes in the spectrograph during the exposure. Its spectrum was determined by two methods : (1) by means of a special cell through which the solution flowed so quickly that only about 1 per cent. was changed photochemically during the exposure ; (2) by the use of solutions containing large amounts of potassium cyanide. If these solutions are illuminated beforehand until the stationary state (under these circumstances of a very weak colour) is reached, the concentration of the nitrile will be constant during the exposure.[7] The amount of coloured leuco cyanide so changed can be determined colorimetrically. Since its extinction coefficient is known, we can correct for this and calculate from the measurements the absorption spectrum of the colourless nitrile. (Equilibrium-method.) Both methods give the same results within the limits of experimental error. Thence also we can conclude that any intermediate product absorbing in a different way (as, e.g., undissociated dyestuff cyanide), if it occurs at all, can only be present in minimal concentrations.

[7] The destruction of the nitrile can be neglected for these weak light-intensities.

Fig. 2 shows the spectral curves for the various solutions expressed as logarithms of the molecular extinction coefficients. $(K = \log \frac{I_0}{I}/Cd$, concentration C in gram mols. per litre, thickness of the layer d in cm.)

From the curves we see that the coloured substance, produced from the leuco cyanide by illumination, possesses the same absorption spectrum as crystal violet, whereas the colourless nitrile form absorbs considerably more strongly in the region 2900 to 2400 Å. The destroyed leuco cyanide shows a diffuse spectrum.

The absorption spectrum of leuco sulphite solution was also determined. It is similar to that of leuco cyanide, but at equal concentration and thickness of the layer the absorption is about a hundred times less.

FIG. 2.

1. Leuco cyanide (not irradiated)   o Equilibrium method.
      ,,   ,,   ,,   ● Flow   ,,
2. Irradiated leuco cyanide ×.
      ,,   crystal violet +.
3. Leuco cyanide destroyed by irradiation.

From these absorption curves various conclusions for the two methods of measurement can be drawn.

(1) *The laboratory method (with pure leuco-cyanide solution)*. We can determine the thickness of the layer which is necessary to absorb 99 per cent. of the radiation to be measured (that is practically quantitatively). Then we can calculate the dyestuff concentration up to which the leuco cyanide solution can be illuminated, without much disturbance of the result of the measurement by the dyestuff formed. Table I. shows these results for the most important mercury lines, for a leuco cyanide solution, saturated at room temperature.

From Table I. it can be seen that the disturbing influence on the experimental results due to the dyestuff formed varies for different wavelengths. This is due to variation of the difference between the extinction coefficients of colourless and illuminated leuco cyanide.

If a Leitz colorimeter is used, the best concentration of the solution for comparison is between 1.5×10^{-6} gram mols. per litre. This also is a reason for illuminating the leuco cyanide solutions only to about this dyestuff concentration.

TABLE I.

Wavelength in Å.	Thickness of the layer of a saturated alcoholic leuco cyanide solution, which absorbs 99 per cent. of the light (in cm.).	Concentration in gram mols. per litre of the dyestuff formed at which the absorption through the dye causes a deviation of — 5 per cent. from the true result.
3130	2·3 cm.	$3·0 . 10^{-6}$
3030	1·3 ,,	$3·5 . 10^{-6}$
2800	·45 ,,	$3·3 . 10^{-5}$
2537	·68 ,,	$1·0 . 10^{-5}$

(2) *The instrument for the measurement of therapeutically active ultra-violet* (leuco sulphite solution + extra sulphite). Here the shape of the curve representing the *sensitivity spectrum* of the test solution is of primary importance, as the therapeutic action also shows a very marked dependence on the wavelength. The conception " therapeutical action " must first be defined more clearly. Ultraviolet light acts on man in very different ways ; a large dose causes a strong reddening of the skin (*erythema*), it browns the skin and further influences the nervous system and the metabolism. These different actions seem to depend in different ways upon spectral conditions. It is clear therefore that a certain measuring instrument can only measure *one* of these actions, since with one light sensitive system it is possible to imitate only one active spectrum. As, on the one hand, the measurement of the radiation which causes *erythema* is of special importance for the prevention of sunburn, and on the other hand, only the sensitivity spectrum of the human skin with regard to this action has so far been adequately studied,[8] we have tried to make the active spectrum of our leuco sulphite solutions conform as much as possible with the sensitivity spectrum of the skin for the formation of *erythema*. Both spectra must match as well as possible, if we wish to compare the same action (in this case the formation of *erythema*) for light of different spectral composition, as for example natural and " artificial " sunlight. This agreement between the two spectra will be obtained by choosing the most suitable thickness of the layer and concentration of the test solutions, bringing it into a tube made of a definite Uviol glass of a definite wall thickness.

Fig. 3 shows this adaption somewhat diagrammetically.[9]

It is possible to make the sensitivity spectrum of the leuco sulphite solution more similar to that of the skin by inserting a Uviol glass filter. The actions in the spectral regions 3200 to 2900 Å. and 2900 to 2500 Å. may be made to have the same ratio for the two curves. The very peculiar form of the curve of spectral sensitivity of the skin makes it improbable that a complete match of the light sensitive systems may be made. This complete match is not necessary, however, as the shape of the sensitivity curve of the skin itself is variable fairly strongly. It depends on the time between the irradiation and the observation of *erythema*, on the place of the skin illuminated and somewhat on the person. The usefulness of a light sensitive system for measuring the action of ultra violet light has to be determined by practical experiments on whether the values so measured agree with the formation of *erythema* by light of

[8] Hausser and Vahle, *Z. Strahlentherapie*, **13**, 41.
[9] Details can be found in *Z. Strahlentherapie*, **38**, 378, 1930 ; E. Weyde, *Über die Grundlagen eines neuen Ultraviolett Messinstrumentes*.

different spectral constitution.   We have carried out these experiments on several persons and obtained satisfactory results.

IV. The Determination of the Quantum Efficiency for the Solution of the Leuco Cyanide of Crystal Violet.

The photochemical change of the nitrile to the cyanide is a comparatively simple process, so that the quantum efficiency would be expected to be a simple number.

The quantum yield was determined for both the lines 3130 Å. and 2537 Å., with a quartz monochromator of medium aperture ($f/5$). The other wavelengths of the lamp used were too weak to be used for a measurement. A horizontal, externally water-cooled, quartz mercury lamp was used (temperature of the water 38°). The advantage of this type is, that the resonance line is obtained at much higher intensity than from uncooled lamps.[10] This source of light had the disadvantage that the intensity, especially of the line 2537 Å., was varying strongly. This did not matter very much, because many measurements could be made. The monochromator was mounted with the exit slit horizontal so that the reaction

Wavelength.
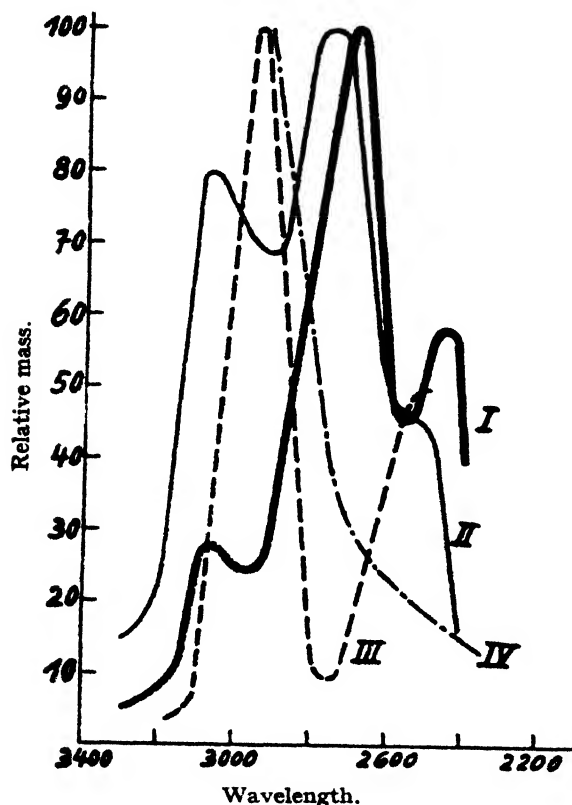
Fig. 3.

1. Leuco sulphite solutions of a definite concentration and in layers of definite thickness.
2. Leuco sulphite solutions behind Uviol glass.
3. Skin sensitivity curve according to Hausser and Vahle.
4. Uviol glass of the thickness used.
   The ordinates show—

Curves I. and II.—The relative quantity of the dyestuff.
   ,,   III.—   ,,   ,, effect on the skin.
   ,,   IV.—The percentage permeability of the glass.

vessel or the thermo couple could simply be placed on top of it.   The reaction vessel was the same as used in the experiments mentioned in Section I. (see under Experimental Method).   The determination of the quantity of dyestuff formed was also carried out in the same way.   The vessel was placed in a cooler, which was filled in most of the experi-

[10] See also W. Frankenburger, *Z. Elektrochem.* **36**, 757, 1930.

ments with a saturated solution of quinine sulphate to absorb stray light which is always present. The energy was measured in the usual way with a thermoelement and mirror galvanometer, calibrated for absolute readings with a Hefner lamp, using Gerlach's values.[11]

Determination of the Quantum Efficiency for the 2537 Å. Line. —The considerable variations of intensity of this line in the source gave rise to a great number of figures. The measurements of energy and chemical reaction were always carried out with only a short interval. Fig. 4 shows the individual results. It is seen clearly that the measurement of the energy and of the dyestuff molecules formed give the same
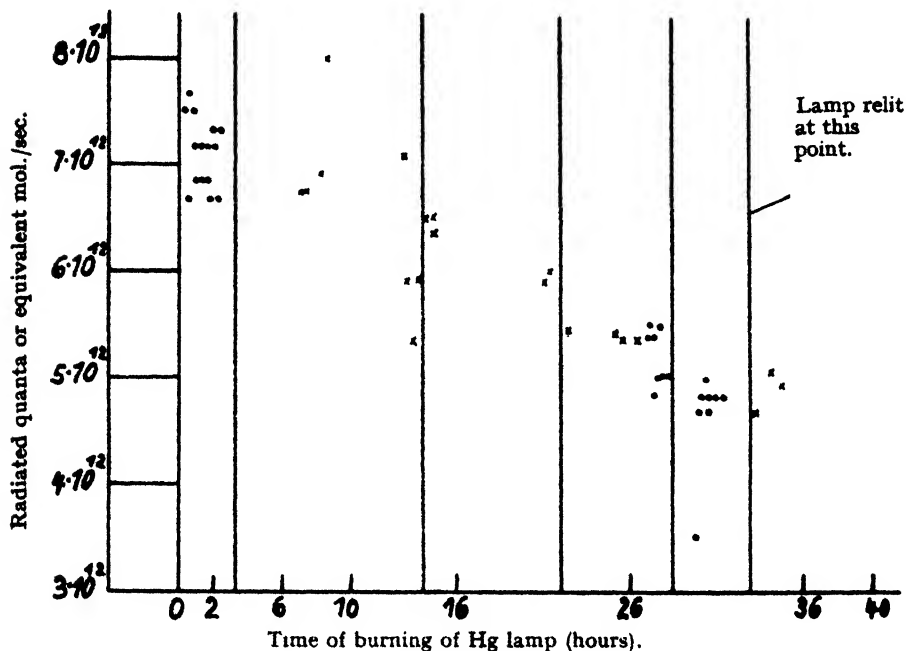
FIG. 4.

Quantum yield for λ 2537 Å.
● Measurements with thermoelement.
×   ,,   ,,   irradiated leuco cyanide.

values, so that the quantum efficiency ϕ of the reaction must be about 1. If one calculates the mean value for the corresponding pairs of determination of energy and yield, it is found that for each quantum absorbed 1·03 molecules of dyestuff are formed. If the mean square error is calculated for the energy measurement (± 4 per cent.) and for the chemical change (± 2 per cent.), the value $1·03 \pm 0·04$ is obtained for ϕ 2537.

Most of the determinations were carried out with saturated leuco cyanide solutions; some with ten times diluted solutions to test the purity of the alcohol used. No differences were found, so long as the layer was made so thick that the product of thickness and concentration was always sufficient to absorb the radiation entirely.* The concentration of the dyestuff formed was always very small (not more than 5 per

cent. of the amount of leuco cyanide) so that its own absorption could not/cause any error. The time of illumination was varied from ten to ninety minutes, the temperature from -6 to $+36°$ C., and the water content of the solutions from 1 to 10 per cent., but no influence could be detected for these factors. Frequent blank control experiments were made, *i.e.*, the reaction vessel with colourless leuco cyanide solution was placed some hours on the monochromator slit, which was then covered with black paper. In these cases not the least colour formation could be observed, proving that no stray light reached the reaction liquid.

The velocity of the reverse dark reaction was very small for the solution used, a reverse change of the coloration only being detectable after some days. From the measurements it was found that only a fraction (6×10^{-7}) of the dyestuff molecules formed is again decolorised per second.

The Determination of the Quantum Efficiency for the 3130 Å. Line.—For these determinations in general, the same is true as for the investigations on the 2537 Å. line. Because of the lower intensity of the 3130 Å. line, somewhat longer times of illumination were necessary, varying from 40 to 150 minutes. As the dyestuff absorbs at this wavelength just as strongly as the nitrile, special care had to be taken to keep its concentration low compared with that of the leuco cyanide. The concentration of the leuco cyanide solution was 5.8×10^{-5} g. mol./litre, the maximum concentration of the dye about 1×10^{-6} gm. mols./litre ; the maximum error caused by the dye is therefore -2 per cent. The source of light did not show the same changes of intensity for the 3130 Å. line as for 2537 Å. Consequently not so many measurements were made. The mean value of six measurements gave for the 3130 Å. line a quantum efficiency of 0.91. The observational errors of individual measurements are larger, since because of the lower intensity, the errors in reading both the energy and chemical reaction are relatively of more importance. Mean errors for the energy measurement of ± 5 per cent. and for the photochemical reaction of ± 9 per cent. are found by the mean square law. The quantum efficiency ϕ 3130 Å. is therefore 0.90 ± 0.1.

From the determination of the quantum efficiency, it can be concluded with great probability that the ratio also equals 1 for all other absorbed wavelengths, since the absorption region of the solution lies mainly between the investigated wavelengths 3130 Å. and 2537 Å. A similarity of the absorption spectrum to the active spectrum can therefore be assumed in this case.

Determination of the Extinction Coefficients for the Lines 3130 Å. and 2537 Å. on the Basis of the Determination of Quantum Efficiency. — It follows from the above investigations that each absorbed quantum forms one dyestuff molecule. If we now use for the determination of quantum efficiency solutions of which the product of concentration and thickness is insufficient for total absorption of the incident quanta, the number of which is known from energy measurements, one can easily calculate how many quanta are absorbed and transmitted, respectively, by the solution. The extinction coefficient can thus also be calculated from these determinations and the values found from spectrograms checked. Some experiments carried out in this way gave the results shown in Table II.

TABLE II.

Wavelength.	Log k $\left(k.C.d = \log \frac{I_0}{I}\right)$ Determined Photochemically.	Determined Spectroscopically.
3130 Å.	$\left\{\begin{matrix}4\cdot05\\4\cdot15\end{matrix}\right\}$ 4·10	4·20
2537 Å.	$\left\{\begin{matrix}4\cdot68\\4\cdot72\\4\cdot65\\4\cdot74\\4\cdot74\end{matrix}\right\}$ 4·70	4·80

The agreement between the values for the extinction coefficients is satisfactory.

Summary.

Our researches showed that the photochemical rearrangement of the leuco compounds of crystal violet can be used for the determination of ultra-violet radiation for two different purposes :—

(1) The pure alcoholic leuco cyanide solution is very suitable for a laboratory method. The amount of dyestuff photochemically formed is, up to a certain degree of conversion, proportional to the intensity of the radiation to be measured. As a result of spectroscopic investigations the thickness of the layer which is sufficient for practically complete absorption of the radiation can be computed for each wavelength, and also the maximum concentration of dyestuff giving no important error by its own absorption. For both wavelengths 2537 and 3130 Å. the quantum efficiency was determined and found to be 1, within the limits of experimental error. When using monochromatic light the leuco cyanide solution can therefore be used for the determination of the absolute energy of radiation from about 3200 to 2400 Å., since each dyestuff molecule formed is known to correspond to one absorbed quantum. Since very small amounts of dyestuff can easily be detected, leuco cyanide solutions are very suitable for the measurement of small intensities of illumination. The reverse reaction of pure leuco cyanide solutions, which would hinder the determination of low intensities, can be prevented to a large extent by the addition of 10 per cent. of water to the solution.

(2) The leuco sulphite solution with an addition which reverses the dyestuff formation, is suitable for an instrument for practical purposes, namely for the doctor, meteorologist, etc., for measuring the physiologically active ultraviolet. These solutions have the advantage that a very large number of measurements can be carried out with the same quantity of solution. It is shown that it is possible to match the sensitivity spectrum of the solution used to the sensitivity spectrum of the skin with regard to formation of erythema and make the dyestuff formation to a certain extent independent of temperature.

We are indebted to Herr Dr. W. Zimmermann, Oppau, for his help with the spectroscopic measurements.

GENERAL DISCUSSION.

Dr. E. G. B. Willey (*London*) said : One of the problems before the physician in giving treatment by Röntgen rays is that of measuring the dosage, all methods as at present applied leaving much to be desired as

regards precision and freedom from errors of observation due to the personal factor. May one ask whether Dr. Frankenburger has been able to apply the technique which he has just described to Rontgen as well as to ultra-violet radiation? Or if changes in colours of dyestuffs cannot be used, could one observe by means of a photo-cell the intensity of fluorescence of a suitable screen exposed to X-rays, and thus obtain a series of standards which, while arbitrary, would nevertheless be free from some of the present objections.

Professor J. Eggert (*Leipzig*), dealing with Dr. Willey's question said : We have given much attention to this problem, but I fear that we shall not readily find a satisfactory solution ; for two reasons.

(1) Despite the great energy content of the rays, the effect of X-rays on matter is not, in our experience, sufficiently strong to serve as a measure of the applied dosage, since the substances tried undergo visible change after quite short exposure. In the researches of Glocker, Günther, and their co-workers, a number of reactions have been experimented upon, but none of these was well adapted for dosage estimation of X-rays in a manner similar to the method whereby Weyde and Frankenburger estimate the actinic characteristics of ultra-violet light.

The conditions of absorption of X-rays are fundamentally different from those of light. X-rays are, as is known, used in two connections : in diagnosis and in therapy ; in the first case we use rays of about 0·5 Å. and in the latter about 0·1 Å. and less. These types of rays are absorbed in profoundly different ways (their absorption coefficients, proportional to about λ^3, are roughly as 1 to 10^3) whilst the biological effects exhibit other fundamental differences (skin and subcutaneous effects).

In my opinion in only one case is it feasible to apply a dosimeter as suggested by Dr. Willey, and that is by the use of the photographic process : for the measurement of the scattered ray, which can be undertaken by the doctor and his staff. It is important to know the extent of this " vagrant " energy because it may easily cause permanent harm to the radiologist (owing to insufficient screening). We have built a dosimeter of this nature ; by reason of the above-mentioned absorption properties of X-rays it is essentially adapted for employment for the purpose of diagnosis (Agfa Röntgen-Film-Dosimeter).

Dr. W. Frankenburger (*Ludwigshafen*) said : With regard to Dr. Willey's question as to whether our method of measurement is suitable for the quantitative determination of the intensity of X-rays, I am bound to answer emphatically in the negative. Our method, using a simple little measuring device which we have constructed as the result of our experiments, is quite specifically only of use for ultra-violet light, and, indeed, only for that spectral region in which the characteristic (erythema-forming) effect of ultra-violet rays is exhibited on the human skin. Neither waves of longer wavelength (such as longer wave ultra-violet, visible, infra-red), nor shorter waves (such as the short wave ultra-violet of the Schumann region, the region of X-rays, etc.), has any effect whatsoever on our apparatus, so that it serves as a quite specific measuring apparatus for the erythema region alone.

GENERAL DISCUSSION.[1]

Professor G. K. Rollefson (*communicated*) wrote : Since writing the paper under discussion Dr. Eyring and I have been investigating, from a theoretical standpoint, the possibility of the existence of Cl_3 in such reaction mixtures. The detailed results are being prepared for publication at the present time, but I can say here that the methods employed are the same as those used by Eyring and Polanyi.[2] The result we have obtained is that Cl_3 is stable with respect to Cl_2 and Cl and furthermore the heat of activation for the formation of Cl_3 is so small and that for the decomposition so large that we must consider that instead of dealing with chlorine atoms in photochemical reactions at room temperature we are dealing with Cl_3. This would mean that the reaction numbered (2) could be replaced by $CO + Cl_3 = COCl + Cl_2$. That is, chlorine molecules will have a specific action which can be duplicated only by molecules capable of forming loose addition products with atomic chlorine. As this is a rather uncommon property, it is not surprising that all the data available at present are satisfied by the assumption of the specific action of chlorine.

With regard to the other point Professor Bodenstein raises, I wish to call attention to the fact that my objections to the consideration of COCl as being at its equilibrium concentration do not depend upon oxygen being in the system. Unless it can be shown that the rate of reaction of COCl with chlorine is slow compared to its decomposition it is not correct to assume equilibrium. Personally I can see no reason for assuming that the reaction of COCl with chlorine would be any slower than the reaction with oxygen.

[1] Continued from page 468.   [2] *Z. physik. Chem.*, **B, 12,** 279, 1931.

REVIEWS OF BOOKS.

Photocells and their Application. By V. K. ZWORYKIN and E. D. WILSON. Pages xi and 209. (New York : John Wiley ; London : Chapman & Hall. 1930. Price 12s. 6d. net.).

The authors are research engineers in the Westinghouse Research Laboratories in East Pittsburgh. Their aim has been to write a little text-book within the understanding of the layman which is not too shallow, nevertheless, for the specialist. They begin with fourteen pages of historical introduction and then discuss general theory after which they discuss the various types of photocell available on the market. Some forty pages are devoted to the applications in the film industry, and in television as well as the many other spheres wherein the cells are now finding use.

Each chapter is provided with a fairly adequate list of references, and at the end of the book there is a bibliography ; the latter would have been more adequate if the dates of publication had been given for all the books to which reference is made.

On the whole, a useful and welcome production.

Artificial Lighting. By M. LUCKIESH. Pp. 254. (London: Crosby Lockwood & Son. 1930. Price 16s. 6d.).

Dr. Luckiesh directs Lighting Research for one of the large American lamp manufacturing concerns. The full title of this book is "Artificial lighting combining radiation for health with light for vision," and the approach to the subject is indicated by the statement that sufficient is now known concerning the biological effects of radiation to warrant " the inauguration of a new era of dual purpose lighting, including radiant energy for health as well as light for vision."

In order to justify this thesis the main facts about light-therapy and erythema, and the results of researches on rickets, ergosterol and vitamin D are recounted. There is a very comprehensive collection of data concerning sunlight, and the book is rich in tabular summaries of the transmissive properties of materials and the physical characteristics of the radiations emitted from various sources. New types of lamps are described, and a chapter on the utilisation of artificial sunlight presents some of the main conclusions.

Whatever the future may have in store in the way of dual purpose lighting, Dr. Luckiesh's book will be useful if only for the clear tables and the seventy odd diagrams and plates which illustrate the text.

R. A. M.

Technical Methods of Chemical Analysis. Edited by C. A. KEANE, D.Sc., Ph.D., and P. C. L. THORNE, M.A., M.Sc., Ph.D. Second Edition, Volume III. (London: Gurney & Jackson. 1931. Pp. xx + 678. Price £3 3s.)

The subjects included in the third volume and the authors responsible for them are as follows: " Clays, Ceramic Products and Refractories " (Chemical Examination—H. V. Thomson) ; Physical Examination –S. R. Hind.) " Glass " —J. D. Cauwood and J. H. Davidson. " Calcareous Cements "—G. Martin and E. A. Bowes. " Drinking Water and Water Supplies and Sewage and Effluents " —Gilbert J. Fowler. " Feed Water for Boilers "—L. O. Newton. " Fertilisers and Feeding Stuffs "—Bernard Dyer. " Soils "—Sir A. D. Hall. " Air "— J. S. Owens and J. H. Coste.

It would, indeed, be difficult to select a group of authorities more fitted for their several tasks than are the collaborators whom the editors were fortunate enough to secure. A comparison of the text with that of the second edition shows that the revision has been so extensive that the book partakes more of the nature of a completely new work than of a mere new edition. This is not altogether surprising since twenty-three years have elapsed since the publication of the second edition and great advances in analytical methods have been made in the interval.

Advantage has been taken of the vast amount of work which has been done in recent years in connection with standardisation of methods of chemical analysis and methods advocated or laid down by such bodies as the British Refractories Research Association, the Institution of Gas Engineers, the U.S. Bureau of Standards, the American Ceramic Society, the British Engineering Standards Association, the American Society for Testing Materials, the Glass Research Association, the Building Research Section and the Atmospheric Pollution Committee of the Department of Scientific and Industrial Research, the Association of Official Agricultural Chemists and the Ministry of Agriculture

have been included. In view of this, the analyst can make use of the methods described with full confidence that they are reliable. A further valuable feature is that in many cases the author of a particular section has amplified the description of a method with information drawn from his own experience. Thus, when alternative methods are described, their relative merits are critically discussed.

The scope of the work is wider than is indicated by the title since, not only does it include methods of chemical analysis, but, in addition, numerous physical methods of examination are described, for instance in connection with cements and refractories. Methods for the examination of the raw materials as well as of the finished products are given.

The examination of glasses provides many problems since in many cases the method has to be modified in accordance with the nature of the oxides present. The section devoted to glasses contains much information on the subject of specifying, colouring and decolorising agents and is, in a limited sense, a treatise on glass manufacture. In the case of ceramic products and refractories, several properties are now capable of precise measurement whereas, formerly, methods were to a large extent crude or empirical. The methods described are based on a wide survey of the literature of the subject.

The book may be warmly commended as a complete and thoroughly up-to-date treatise and deserves a large sale.

Tables Annuelles de Constantes et Données numeriqués. Vol. VII, 2nd part. Index for 1910-1922. (Gauthier-Villars, Paris.)

The second part of volume seven contains the data on Dielectric constants, Magnetism, Radioelectricity, Cryoscopy, Diffusion, Solubility, Chemical Equilibria, Photochemistry, Conductivity and electromotive forces of electrolytes, Colloids, Adsorption, Crystallography (including X-ray analysis), Organic chemistry (Oils, Fats, Waxes), Biology, Engineering and Metallurgy. These are contained in about one thousand quarto pages. As to which of these subjects is the most important is a question for the reader to decide. Probably no part is more important and interesting than that on dielectric constants which gives with diagrams an account of modern work on the variation of these constants with temperature.

The index to vols. I. to V. has long been needed. It forms a volume of 382 pages. The index is divided into three parts ; (i) an analytical, (ii) an alphabetical, and (iii) a formula index. The analytical is an amalgamation (in four languages) of the subject indices published in the successive volumes. The alphabetical index gives the names of vegetable or animal species, of various substances with or without definite formulæ, followed in the last case by their empirical formulæ. The third index contains their formulæ arranged according to an early understood system and the page references concerning them. A little practice will enable any one easily to find the matter of the tables in which he is interested.

Particulars of price, etc., can be obtained from M. le Professeur Ch. Marie, 9, rue de Bagneux, Paris VIe.

Elektrophorese, Elektro-osmose, Elektrodialyse in Flüssigkeiten. By
  P. H. Prausnitz and J. Reitstoetter. (Dresden and Leipzig : Theodor
  Steinkopff, 1931. Pp. xii + 307. Price Rm. 20 net.).

This volume is one of the series of *Wissenschaftliche Forschungsberichte*
published under the general editorship of Dr. R. E. Liesegang. The authors
who have both had unusual experience of the technical applications of electro-
osmosis, etc., say in the preface : " Everyone who has been confronted with the
task of attacking a problem arising from the practical requirements of everyday
life will have observed that, especially in fields where rapid advances are still
being made, several lines of investigation run along one another—which in
itself is not astonishing—which, however, take no notice of one another, as if there
were no other ways at all, and which but rarely make the attempt to utilize the
experiences gained by others in developing their own work." Certainly this
seems to be the case to a very striking degree with the phenomena due to
potential differences at interfaces, and the reader who knows only the textbooks,
or has made occasional use of cataphoresis in the laboratory, will be surprised at
the number of technical applications which have been contemplated or, at any
rate, patented.

The authors deal with both theory and practical application—whether on a
laboratory or on a technical scale—in the concise manner of the whole series of
" reports," but adequately and critically.   In the theoretical portion the reviewer
has noticed one omission only : the authors attach considerable importance to
R. H. Humphry's method of determining the charge on particles of organosols
(allowing a jet of the sol to flow into the dispersion medium in a strong field and
noting the movement of the jet towards either electrode.[1] They appear to have
overlooked a serious criticism of this method by E. H. Buchner and A. H. H.
van Royen,[2] who show conclusively that the movement of the jet is not due to
charges on the disperse particles in it, but is caused by the difference in con-
ductivity between the sol and the dispersion medium which cause potential differ-
ences at the boundaries of the jet which face the electrodes.

The descriptions of technical processes and apparatus give the satisfactory
impression that the authors are not merely abstracting the literature but have
personal experience of much of what they describe.   Particularly is this the case
in the sections on electro-osmosis, which contain much very curious information,
e.g., on the effects due to the charges on the diaphragm, which determine both
the rate of osmosis and the final reaction of the dialysate to an unexpected
extent.

In addition to very copious references in the text and numerous abstracts of
patent specifications the book contains a bibliography of papers not otherwise
mentioned and a complete register of patents.   It fills a gap in the literature of
colloids and may, incidentally, play a useful part in supplying lecturers con-
ronted with the task of illustrating the " practical " applications of colloid science
with some unfamiliar instances.

[1] *Trans. Far. Soc.*, **22**, 420, 1926.   [2] *Koll. Zeitschr.*, **49**, 249, 1929.

                                                          E. H.

AN AIR THERMOSTAT FOR QUANTITATIVE LABORATORY WORK.*

THE QUANTITATIVE HUMIDIFICATION OF AIR IN LABORATORY EXPERIMENTS.†

DISCUSSION.

(At a meeting of the Faraday Society held on 10th June, 1931.)

Mr. U. R. Evans (*Cambridge*), said: Dr. Vernon's thermostat has several most valuable features, to the practical utility of which I can bear testimony, having copied several of them in an air thermostat recently erected at Cambridge. There is, however, one feature which, whilst probably involving no error in the class of work on which Dr. Vernon is engaged, might be a source of danger in certain experiments on wet corrosion. The distribution of corrosion on a vertical iron specimen in an unstirred potassium chloride solution, for instance, is very susceptible to slight movement in the liquid. So long as stagnancy is maintained, the anodic area below and cathodic area above are, on a carefully prepared specimen, separated by an absolutely horizontal boundary. Even slight vibration from a motor may, however, interfere with the "ideal" distribution of the areas—a disturbance which Mr. T. P. Hoar has found it possible to eliminate by means of sorbose rubber or felt. For such experiments, it would seem unwise to use an incandescent filament heater which, by causing the liquid to become slightly hotter on one side than on the other, might set up convection current in the vessel. The liability to this danger cannot be tested by taking thermometer readings—however accurately—in different parts of the cupboard, since the thermometer does not indicate whether it is receiving its heat uniformly from all sides, or from one side more than from the other. No doubt, in Dr. Vernon's thermostat it is not intended to heat the specimens by radiation, and probably *most* of the heat-transfer does occur by means of the air-current; unfortunately, if the thermostat contains an incandescent heater several hundred degrees above the temperature of the specimens, it is quite inevitable that some radiation *must* pass from the hot to the cold body.

Dr. Vernon has recognised this fact when he says that "attention has been concentrated upon the symmetrical arrangement of the heating system." Unfortunately it is impossible to arrange eight lamps in such a way that the radiation density falling on a given surface is independent of the inclination of that surface. Certainly, however, eight little lamps will cause less disturbance than one big one A single heating element at temperature $T°$ above the experimental temperature will cause more con-vection than 8 elements at temperature $T/8$, although both arrangements should provide the same heating; 100 elements at temperature $T/100$ will

be better still, whilst theory suggests that the ideal arrangement would be an infinite number of elements at a temperature infinitesimally in excess of the experimental temperature. This is the principle which we have aimed at using in the thermostat at Cambridge, where the chamber contains no heating element, but is surrounded by metal walls kept at a temperature sensibly the same as that of the experiment. Under these conditions, no appreciable transfer of heat by radiation is likely to occur ; the whole heat-transfer will take place by means of the air-current through the chamber. If once, however, an incandescent type of heater is introduced into a thermostat, some radiation transfer is quite inevitable. If an internal heater is required, it should be of the wire *or* gauze type which is kept only a few degrees above that of the experiment—as, for instance, in Dr. Fox's thermostat.

For another and quite different reason, radiation-heating may cause an error. The constant temperature assumed by any body in the cupboard is that temperature at which the body will gain heat as quickly as it loses heat. If the system in the cupboard is isothermal, this will be independent of the radiation constants of the various bodies, and the thermometer, the thermo-regulator, and the experimental specimens will all come to the same temperature. But if the system is *not* isothermal, and if the transfer of heat occurs partly by radiation and partly by means of the air current, there is no guarantee that the thermometer, the thermo-regulator, and the experi-mental specimen will come to the same temperature ; thus there is a danger of an error, which is in no way gauged by measurements of tempera-tures taken with the same thermometer at different times and at different places.

I am not suggesting that Dr. Vernon's work is vitiated in this way, but I would venture to urge those who contemplate a thermostat for wet corro-sion work to consider these points. The actual constancy of temperature in Dr. Vernon's thermostat is a matter for congratulation, and suggests that it would be useful for studying reactions where the temperature coefficient is high. Actually in most corrosion reactions the temperature coefficient is very low ; in the attack of iodine (in chloroform solution) on silver the rate is only twice as great as $35°$ C. as at $0°$ C.[1] For such reactions, a very close temperature control is not needed. Where a very close temperature control is called for, it will perhaps be most conveniently obtained by using the principle of Tian's [2] method, which depends on using a large number of vessels one inside the other ; by means of such a device, Mr. Ward,[3] in the Physical Chemistry Laboratory at Cambridge, recently succeeded in reducing the temperature variations to $0·0000017°$ C. Per-sonally, I have no experience of this method ; in our own corrosion work we do frequently use one vessel inside another, but this is for a different purpose.

Dr. A. R. Lee (*London*) said: Dr. Vernon is to be congratulated on attaining, with a maximum simplicity of construction, a constancy of tem-perature of the order of one-hundredth of a degree, constant with respect to both time and space. Good results with an air-thermostat are much more difficult to obtain than with a water thermostat, owing to the small thermal capacity of the air; the chief difficulty is to obtain the same temperature at different points in the enclosure. Dr. Vernon seems to have achieved this to a satisfactory degree by efficient mixing of the air

[1] U. R. Evans and L. C. Bannister, *Proc. Roy. Soc.* (**A**), **125**, 370, 1929.
[2] A. Tian, *J. Chim. Phys.* **20**, 132, 1923.
[3] A. F. H. Ward, *Proc. Cambridge Phil. Soc.*, **26**, 278, 1930.

and careful avoidance of a continuous uni-directional flow across the working space.

I should like to ask if the recorded temperatures remain the same when the bell jars are in position and if any temperature difference has been observed across the diameter of any one bell jar.

It is well known that if constant temperature is required over a spatial interval in an air thermostat it is essential to avoid uni-directional flow, as not only is a temperature gradient set up in the space by the air-stream itself, which is continuously losing heat, but objects placed in the path of the stream will have gradients within themselves because they receive heat from one side only, the lee side always having a pocket of stagnant air next to it. The adoption of this principle places Dr. Vernon's thermostat in a category above those in which it is not employed.

I would suggest that with experiments such as immersed corrosion, where it is important to ensure freedom from the errors inherent in an air thermostat, the only safe method is to use a water thermostat in which all moving apparatus is mounted independently of the thermostat.

The President asked where Dr. Vernon had placed his thermometric devices and what steps he had taken to satisfy himself that there was uniformity of temperature at all parts of the thermostat. He would suggest for instance that wherever there was an obstruction, such as a bell jar, there would probably be eddies formed.

Mr. J. H. Coste (*London*) said: The thermostat should be of use in work which necessitates the weighing of glass apparatus as it would overcome the uncertainty of the hygroscopic state of the surfaces which was usually sought to be done by wiping and leaving for a time before weighing.

The humidifying apparatus would be very suitable if it were desired to redetermine the saturation values for aqueous vapour in air. The difficulty of obtaining complete saturation of air with water was a good example of the general difficulty due to the slowness of exchanges around the saturation point experienced in all cases where it was sought to saturate one phase with another, which was one of the principal reasons for the differences in the results of different workers for the solubility of gases in water and other liquids.

Dr. Vernon, in reply, wrote: Probably the major issue was raised by Mr. Evans when he referred, among a number of interesting points, to errors which may occur in the air thermostat through radiation from the source of heat employed. In my view, this matter must be considered in relation with errors arising from convection processes, since obviously each of these types of error is equally important and will give rise to similar effects in vessels placed within the thermostat. Mr. Evans considers that, in the thermostat described in the paper, errors due to radiation are appreciable, notwithstanding that they are not made evident by readings on the Beckmann thermometer. Whatever shortcomings may be alleged against the thermometer in respect to radiation heating, these clearly do not apply to convection heating; and Mr. Evans evidently accepts the (spatial) constancy of the thermometer readings as demonstrating a corresponding freedom from errors of the convection type. (Known disturbances in the thermostating conditions, even of a most trivial character, are in fact, accompanied by an immediate response on the part of the thermometer.) The point that I wish to emphasise is that even if one succeeds in eliminating errors due to radiation, and yet ignores completely the effects of convection, then the errors introduced on the one hand may be of a much grosser order of magnitude than the errors eliminated on the other. In the

thermostat described, the risk of radiation error (assumed to be undetectable by the thermometer) may presumably be reduced to negligible dimensions by the simple expedient of substituting heaters of the wire grid type for the filament lamps at present used. Originally, indeed, it had been intended to use heaters of this type, and the lamp method was only adopted from the point of view of eliminating fire risks. Nevertheless, experience with the method has given no cause for regretting the change of plans ; the use of filament lamps has the merit of great convenience, combined with an extremely rapid response to the rise and fall of the mercury in the regulator column. At the same time I fully agree with Mr. Evans that a radiation error which may be negligible (or even beneficial through facilitating the mixing of the gas in the bell-jar) in our work, may become serious in other classes of work. Whilst also freely admitting the validity of the theoretical objections that Mr. Evans has raised against the use of incandescent heater lamps, I am a little doubtful why thermometers in different parts of the cupboard (as distinct from a single thermometer in a fixed position) should entirely fail to detect the error of which he complains ; and I cannot help feeling that the error must be very small in practice. However, the change from filament lamps to wire grids could be effected without any modification of the general design of the thermostat.

Mr. Evans has pointed out the danger that would arise from the use of a single source of heat within the cupboard. I would suggest that this danger is not eliminated merely by placing the source of heat outside the cupboard ; the type of error may be changed but its magnitude is not necessarily affected. Heat is carried into the cupboard by means of the air stream ; if this is uni-directional, as in the thermostat described by Mr. Evans, then, as Dr. Lee has pointed out, the temperature gradient in the air stream must affect not only the cupboard as a whole, but also objects or vessels placed therein. Moreover, if the air stream passes through only a portion of the thermostat chamber, " dead spaces " must result. If the doors of the cupboard are opened at all frequently, it is not sufficient to assume that objects contained in these dead spaces will assume the temperature of the walls, unless, indeed, the air in the outer room is also thermostated.[4]

In the light of the present discussion, some approach to the ideal arrangement should be attained by combining the advantages of the two systems, i.e., by ensuring that the space between the double walls really is efficiently thermostated and also that the whole of the air in the inner chamber is thoroughly stirred. The former desideratum might be effected by converting the double walls into a water thermostat, the temperature control being obtained by regulators in the inner chamber.

The question of vibration of the thermostat cupboard is really superimposed upon that of its behaviour as a thermostat. Thus, thorough stirring of the air, while essential to good thermostating, obviously militates against freedom from vibration. In atmospheric corrosion experiments, as Mr. Evans has observed, vibration has no prejudicial effect. In immersed

[4] Thermostating of the outer (room) air is employed in connexion with a (double-walled) air thermostat devised by Messrs. F. A. Gould, J. C. Evans, and H. Barrell of the Metrology Department, National Physical Laboratory, where it is doing very accurate service. The present work was completed without knowledge of this much more elaborate apparatus, a description of which has still to be published. Through the courtesy of the gentlemen named, I have lately had the opportunity of inspecting their thermostat. Whilst I do not wish to forestall in any way their own account of their work, it is noteworthy, as bearing upon the present discussion, that their system involves the thorough mixing of the air in the inner chamber.

corrosion, on the other hand, as Mr. Evans has himself shown and as already shown by Dr. Bengough and his collaborators,[b] vibration may have a profound effect. In such cases, as Dr. Lee has pointed out, the water thermostat is to be preferred, unless its use is precluded by other circumstances.

In reply to Dr. Lee's question, further information has now been obtained with regard to thermometer readings in different parts of the cupboard, both with and without the bell-jars. The data are incorporated in the following diagrams, the positions of the figures corresponding with the positions of the thermometer in the thermostat. The thermometer was allowed to remain in each position for 15 minutes before the reading was

READINGS ON BECKMANN THERMOMETER (BLACKENED BULB).

CONTROL TEMPERATURE OF THERMOSTAT · = 25°C.

(1). WITH BELL-JARS IN POSITION :-
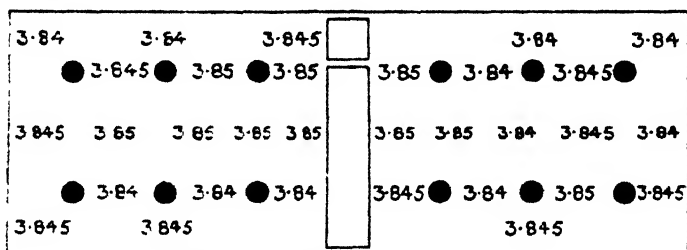
(2) WITH BELL-JARS REMOVED -
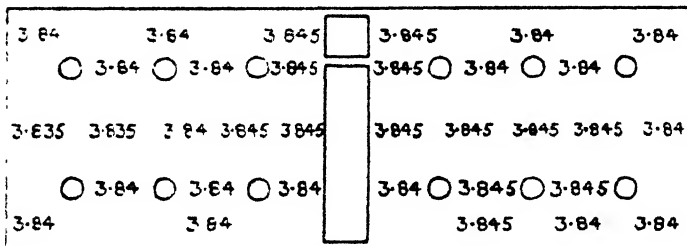
Fig. 1.

taken ; for this purpose the bulb of the thermometer was blackened with (turpentine) soot in order to facilitate absorption of radiant heat.

It will be seen that the readings in the two cases are almost identical, showing that there is no appreciable screening effect of one bell-jar upon another. The constancy of the readings on the black-bulb thermometer in different parts of the cupboard suggests, moreover, that errors due to radiation must be correspondingly small. These results also provide the information asked for by the President. The freedom from error of the type described by the President is no doubt due to the fact that the bell-jars are not in direct line with the primary air streams. Since these meet above the bell-jars, the result is a downward streaming over and between

[b] Bengough, Stuart, and Lee, *Proc. Roy. Soc.*, **127 A**, 51, 1930.

the vessels, the streams returning in opposite directions along the floor of the cupboard (beneath the bell-jars).

I wish to convey to Mr. Coste, on behalf of Mr. Whitby and myself, our appreciation of his reference to the method of humidification described in the second paper. In our work we had no intention of competing with classical methods; all that is claimed (besides a reasonable degree of accuracy) is rapidity and compactness —factors that are hardly compatible with more elaborate apparatus.

A LABORATORY STUDY OF THE ATMOSPHERIC CORROSION OF METALS.*

DISCUSSION.

(At a Meeting of the Faraday Society held on 10th July, 1931.)

Dr. W. H. J. Vernon in presenting the paper said (in amplification of the paper): Since the publication of the paper, additional data have been obtained which appear to have interesting implications.

With reference to Fig. 11 an additional point has been determined

(5·1 mg. per sq. dm. at 0·75 per cent. SO_2, 99 per cent. relative humidity). This is now plotted in Fig. 18, in which a fair curve is drawn through the points on each side of the minimum, the position of which is thus defined more clearly than in Fig. 11. The point of intersection of the two branches marks both the minimum corrosion value and also the critical concentration of sulphur dioxide, the latter value being very nearly 0·85 per cent.
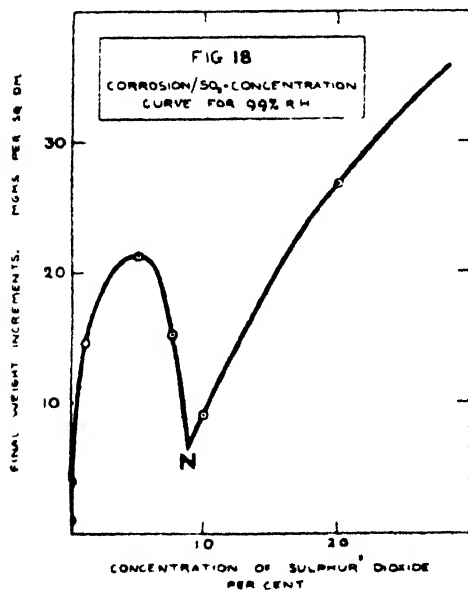
With reference to the Table on p. 265, further analytical results have been obtained for the products from atmospheres containing 0·1 per cent. and 0·75 per cent. sulphur dioxide (99 per cent. relative humidity). In the original table the calculated formula in each of the last three examples was incorrect with respect to the figure denoting molecular parts of H_2SO_4; the figures should read respectively 0·08, 0·52 and 1·87. The completed (and corrected) results are given in Table I.

In Fig. 19 the molecular parts of either base or acid associated with one molecular part of normal salt in the product are plotted against concentration of sulphur dioxide in the atmosphere. The intersection of the two branches (at N) marks the point of complete normality; the concen-

TABLE I.

Per Cent. SO₂ in Atmosphere.	Ratio of SO₄ to Cu in Product.	Calculated Formula of Product.
0·1	1·02	$CuSO_4 + 0·48\ Cu(OH)_2$
0·5	1·16	$CuSO_4 + 0·32\ Cu(OH)_2$
0·75	1·35	$CuSO_4 + 0·12\ Cu(OH)_2$
1·0	1·63	$CuSO_4 + 0·08\ H_2SO_4$
2·0	2·30	$CuSO_4 + 0·52\ H_2SO_4$
4·0	4·33	$CuSO_4 + 1·87\ H_2SO_4$

tration of sulphur dioxide at which this occurs is again very nearly 0·85 per cent. Clearly, this concentration is a critical one both with respect to the corrosion of the metal and also the composition of the product. Thus, at the minimum point in Fig. 18 the product consists entirely of normal copper sulphate.

At concentrations of sulphur dioxide less than 0·85 per cent. basic copper sulphate enters into the composition of the product. Corrosion rises to a maximum at approximately 0·5 per cent. SO_2 and then falls off steadily at lower concentrations. Over the corresponding portion of the curve representing composition of product, however, from 0·85 per cent. down to 0·01 per cent. SO_2 (the lowest concentration investigated) there is no further point of inflexion. Nevertheless, at still lower concentrations it is evident that a sharp

FIG 19
COMPOSITION OF CORROSION PRODUCT IN RELATION TO CONCENTRATION OF SO_2 IN ATMOSPHERE

break in the curve must occur, for when the SO_2 concentration is zero the value of y (excess of base over normal salt) must be infinity. It is now suggested that this (hypothetical) break in the curve (M in Fig. 19) marks the point at which the product consists wholly of a basic copper sulphate having the highest possible degree of basicity. According to the co-ordination theory, maximum basicity is given by the formula $[Cu\{(HO)_2Cu\}_3]SO_4$, or $CuSO_4 . 3Cu(OH)_2$. The stability of such a compound in atmospheric corrosion products was predicted by Professor G. T. Morgan and has been amply confirmed by analyses of products from copper structures after long exposure in the field; among the various products examined the basicity given by the formula was never exceeded.[1]

On the foregoing hypothesis there are thus three ranges, within each of which the product consists of a mixture of two constituents; in Fig. 19 these are represented as follows: BM, free base and basic sulphate; MN, basic sulphate and normal sulphate; NA, normal sulphate and free acid.
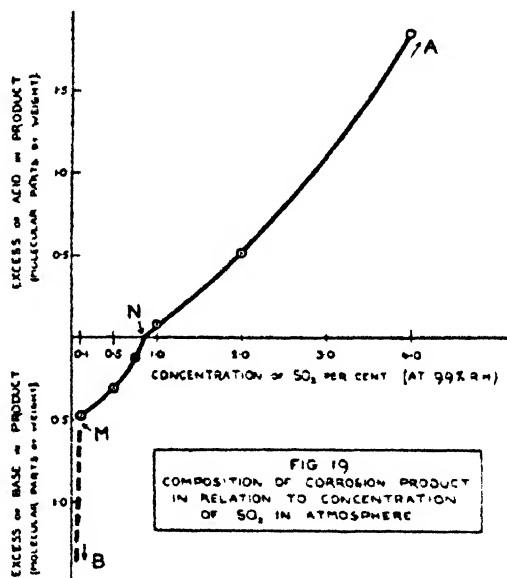
[1] Vernon and Whitby, *J. Inst. Metals*, 44, 389, 1930.

It is further suggested that, as the point of inflexion N in Fig. 19 is correlated with the minimum point in the corrosion curve, at which point the product consists wholly of normal sulphate, so the (hypothetical) point of inflexion at M should be correlated with a similar minimum corrosion value at which the product consists wholly of basic sulphate. This minimum point is not realised in the experimental curve (Fig. 18) owing, no doubt, to the smallness of the values concerned. It is indicated schematically at M' in Fig. 20, where (in relation to the established minimum at N') its probable distance from both the vertical and horizontal axes is necessarily exaggerated.

The depression in the corrosion value toward the minimum point at N' (and hypothetically at M') is clearly to be associated with the concentration of sulphur dioxide reaching an optimum value for the formation of a definite chemical compound at that point. Initially, as would be expected, the rate of attack is actually greater in the neighbourhood of the critical concentration. This may be seen by reference to Figs. 6 and 8 (p. 262) in which are shown the curves for 0·1 and 1·0 per cent. sulphur dioxide respectively (see especially curves for atmospheres of 99 per cent. relative humidity). Comparison with Fig. 7 (0·5 per cent. SO_2) shows that the initial rate is definitely greater in each case than it is at the intermediate concentration (corresponding with the peak of the curve in Fig. 20). This greater initial rate, however, is followed by a more rapid "flattening" of the curve toward the time axis; equilibrium is reached more quickly and the final corrosion value is not so great. Clearly, it is the more rapid covering of the metal surface with a chemically stable product that accounts for the minimum corrosion value at the critical concentration.
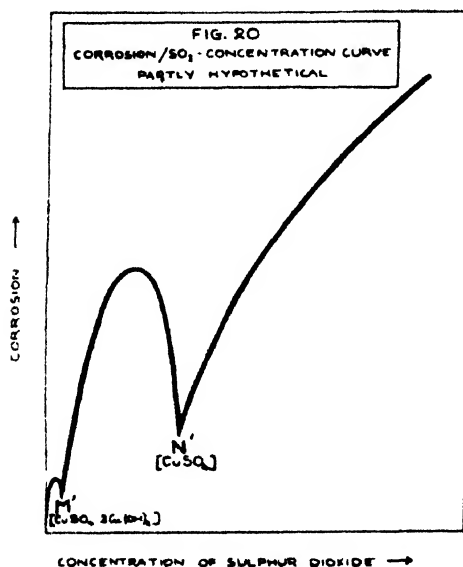
FIG. 20
CORROSION/SO₂ - CONCENTRATION CURVE
PARTLY HYPOTHETICAL

CORROSION

N'
[CuSO₄]

M'
[CuSO₄ 3Cu(OH)₂]

CONCENTRATION OF SULPHUR DIOXIDE →

Finally, it may be expected that the range MN in Fig. 19 (M'N' in Fig. 20) will correspond to the range within which the green patina of basic copper sulphate may be developed in actual service. For on complete exposure to the open air the associated normal sulphate will be gradually removed by rain, leaving the residue progressively richer in insoluble basic sulphate. This progressive increase in basicity has been observed experimentally, both in field tests at South Kensington [2] and also by examination of products representing various periods of exposure of actual copper structures.[1] It is probable, however, that at low concentrations of sulphur dioxide a certain amount of the increase in basicity is brought about by the gradual hydrolysis of the normal copper sulphate associated with excess of base, quite independently of the leaching action of rain. Thus, an experiment has been carried out in an atmosphere containing 0·1 per cent. sulphur dioxide (99 per cent. relative humidity) in which the composition

[2] Vernon, " Second Report," *Trans. Faraday Soc.*, **23**, 177, 1927.

of the product was determined at intervals. The results are given in Table II., from which the increase in basicity during the period of the experiment will be apparent.

TABLE II.

Period of Exposure. Days.	Ratio of SO₄ to Cu in Product.	Calculated Formula of Product.
11	1·12	$CuSO_4$ 0·26 $Cu(OH)_2$
20	1·05	$CuSO_4$ 0·36 $Cu(OH)_2$
30	1·01	$CuSO_4$ 0·48 $Cu(OH)_2$

In conclusion, Dr. Vernon expressed his indebtedness to Messrs. Printers Plates, Ltd., who had kindly presented a number of plates of electrolytic copper, which, on account of their specially fine surface, had proved most useful in the experiments; he regretted that this acknowledgment had been inadvertently omitted from the acknowledgments given at the end of the paper.

Dr. R. S. Hutton, after expressing his gratification that the work which had originated in the Atmospheric Corrosion Research of the British Non-Ferrous Metals Research Association was still being actively pursued, referred to the results with emeried and sand-blasted specimens respectively. He suggested that possibly the differences observed may be due to a certain amount of oxidation during the rubbing with emery paper. The temperature might be raised sufficiently to cause the oxide film to reach the critical thickness which had been demonstrated in Dr. Vernon's previous work. On the other hand this effect would be absent from the sand-blasted specimens since no appreciable heating would take place during treatment.

Dr. W. S. Patterson (*London*) said : One of the fundamental facts which emerges from Dr. Vernon's work is the principle of "Critical Humidity" in relation to atmospheric corrosion. Dr. Vernon has shown in the present and in previous reports that there are definite humidities above or below which corrosion is increased or diminished. In the case of the metal iron the phenomenon is very remarkable, and the writer has put forward a possible explanation based on the colloidal properties of rust.

The fact that critical humidities relative to corrosion, do exist indicates that changes are taking place at such humidities in the physical or chemical characteristics of the corrosion products. In the case of copper the scale formed during corrosion appears to be continuous in contrast to the non-continuous porous type of scale formed on iron or zinc.

It is not surprising that in the case of copper Dr. Vernon has found the explanation of the critical humidity effect can be related to the formation of definite chemical compounds. It may well be, however, that in the case of both zinc and iron the explanation of the critical humidity effects lies in the physical characteristics of the scale.

In view of the known colloidal properties of zinc hydroxide it is possible that a similar type of action to that suggested by the writer for iron is occurring, and there is already a substantial amount of evidence in proof of this.

Mr. U. R. Evans (*Cambridge*) said : Dr. Vernon is to be congratulated on this remarkably fine piece of work. The action of air containing sulphur dioxide and moisture on copper presents some similarities, but also some interesting differences to the action of similar gas mixtures on

iron, which I studied qualitatively some years ago.[3] Perfectly dry air containing sulphur dioxide leaves iron absolutely bright and unchanged even after a month's exposure, but small amounts of moisture, far below saturation point, permit a rapid action. The attack, however, is not uniform ; there is some general attack, but there remain numerous circles completely bright and unattacked, and at the centre of each is a dark spot representing a pit; evidently this is a weak point on the primary film, and the immune area of wonderfully perfect circular form is the zone of cathodic protection ; under some conditions, rings of corrosion-product are formed, either through exuding from a pit, or possibly surrounding some cathodic particle. Whatever the exact interpretation, the whole aspect strongly suggests electrochemical action. But on copper, nothing of this sort was observed, and I gather that Dr. Vernon regards the attack as a direct one—only electrical in the sense that all chemical actions are electrical.

Probably he is right. The main reason why an electrochemical mechanism—depending on spatially separated anodic and cathodic areas— so often appears in corrosion studies, is simply that direct combination with oxygen will usually tend to bring the action to an end, since the oxide, formed in situ, interferes with access of oxygen to the unchanged metal below ; the indirect electrochemical mechanism leads to the production of the oxide in hydrated form at a sensible distance from the point of attack, and it will usually be non-protective. Thus the direct chemical action, although indicated as possible from considerations of energy, is brought to a standstill from consideration of geometry, whilst the electro-chemical action can proceed unchecked. These factors will influence the course of corrosion most strongly in the case of iron ; on copper, especially if sulphur compounds are present, the directly formed film is permeable to the reacting bodies, as is seen from the fact that air, containing hydrogen sulphide rapidly produces interference colours on copper at ordinary temperatures, although air free from hydrogen sulphide causes no change unless the temperature is raised sufficiently for oxygen to diffuse through the oxide film, when the same colour-sequence appears. Thus probably the attack upon copper by Dr. Vernon's gas mixture will be a direct one, limited in velocity by the rate of diffusion through the layer of products ; and the important part played by these products in limiting the rate of attack is shown not only by the shape of the time corrosion curves, but also by the fact that the rate is minimal at just that concentration of sulphur dioxide which causes the composition of the product to be exactly $CuSO_4$, with excess neither of H_2SO_4 nor $Cu(OH)_2$.

Dr. A. R. Lee said : Dr. Vernon is maintaining the high standard of quantitative accuracy which has always characterised his work in the past. This is shown very effectively by the manner in which the quantities taken from entirely different sets of experiments conform to smooth curves. He is to be congratulated as it is only by such methods that future advance can be made in the solution of problems of either atmospheric or immersed corrosion.

The experiments with the sand blasted specimens have given very interesting results. The relatively small increase in corrosion on these specimens in hydrogen sulphide atmospheres suggests that the protective film can form with as much ease and effect over the roughened surface as it can over the relatively smooth metal. I should like to ask if Dr.

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[3] *Trans. Amer. Electrochem. Soc.,* **46,** 247, 1924.

Vernon's experience on protective films has led him to form any opinion as to the ease or difficulty with which such a film will form at a sharp edge of the metal.

Dr. A. R. Martin (*London*) (*communicated 22nd June*) wrote: Dr. Vernon suggests that in atmospheres containing less than the critical concentration of sulphur dioxide oxidation of SO_2 to SO_3 is catalysed at the surface of the specimen by metallic copper, and that in the presence of oxygen $CuSO_4$ is formed. He brings forward no evidence for the existence of a catalytic action, and in the light of the work of Constable [4] it appears unlikely that the copper in his specimens would be catalytically active. Furthermore, if his view be correct, why is water vapour necessary for the corrosion of copper? Surely sulphur dioxide dissolves in an adsorbed film of water to form H_2SO_3, which is oxidised by aerial oxygen to H_2SO_4. In this connection it is interesting to note that Titoff [5] observed that traces of copper sulphate accelerate the oxidation of sulphite solutions.

The existence of the critical humidity might be explained by the hypothesis that it corresponds to the partial vapour pressure of water over the most concave surfaces of liquid water condensed in irregularities of the surface of the specimen. Below the critical humidity the only water available for the formation of sulphuric acid is that adsorbed by the field of force at the surface of the specimen. Above the critical humidity "capillary" condensation can occur, resulting in a greatly increased supply of water, and hence enhanced corrosion. This hypothesis explains the greater effect of relative humidity in the case of the sand-blasted specimens. It would be interesting to know the effect of relative humidity on the corrosion of mirror-polished specimens.

Dr. J. C. Hudson (*Birmingham*), wrote: I welcome this paper from Dr. Vernon as a very valuable contribution to our knowledge of the atmospheric corrosion of metals. For the first time, quantitative results have been obtained for the atmospheric corrosion of a metal under absolutely defined conditions that any other investigator should be able to reproduce; I congratulate Dr. Vernon most heartily on this achievement, and look forward to an extension of his work to other metals. In this connection, I think it would be an advantage if some, if not all, of the results shown graphically in Figs. 3 to 10 could be placed on record in tabular form. These results are absolute and fundamental; as regards correlation with future researches, it is no longer a question of the shapes of the curves but of the actual values obtained, which can be but tediously and imperfectly estimated from graphs.

There are two points that I should like to raise; the first refers to the question of the critical humidity. Dr. Vernon's experimental results clearly show the existence of a critical humidity lying between 63 and 75 per cent., above which there is a marked increase in the rate of attack on copper by the sulphur dioxide atmospheres under consideration. This at first sight appears to be at variance with my own work on the critical humidity of various corrosion products,[6] in which I assigned a higher value (> 85 per cent.) to copper. I was, however, using the term "critical humidity" in a somewhat different sense, to denote that humidity at which tangible condensation of moisture occurs on the specimen, with the result that corrosion then proceeds at a metal-liquid interface, as distinct to a metal-air interface below this critical humidity. Dr. Vernon does not

[4] *Proc. Roy. Soc.*, A, 110, 283, 1926.   [5] *Z. physikal. Chem.*, 45, 641, 1903.
[6] *Trans. Faraday Soc.*, 25, 204, 1929.

record the appearance of visible moisture on any specimens, even at 100 per cent. relative humidity. I shall be interested to learn whether any such condensation occurred, and consider it probable that in similar tests on other metals, such as zinc and nickel, moisture would have been deposited at much lower humidities. There is, of course, no reason why there should not be several critical humidities for a given metal, if the critical humidity is defined as that at which there is a discontinuity in the corrosion velocity/humidity curve.

With reference to the experiments on the behaviour of corrosion products from H.C. and arsenical copper (pp. 269-272), Dr. Vernon concludes that the product from the former has a greater hygroscopicity and is more susceptible to changes taking place at the critical humidity. I assume that Dr. Vernon does not wish to convey the impression that the critical humidity is lower in the case of the purer copper, but that, under equivalent conditions, it absorbs a relatively larger amount of water, since it does not follow that if one corrosion product absorbs relatively more moisture than another, its critical humidity is necessarily higher. (The critical humidity is, of course, indicated by the appearance of a marked change in the direction of the moisture absorbed/humidity curve, and is clearly independent of the absolute magnitude of the ordinates.) In the present case, the facts agree with the conclusion that there is a difference in the composition of the corrosion products on H.C. and arsenical copper. A compound rich in arsenic is known to accumulate on the latter, and, if this is assumed to have a higher critical humidity or to absorb less moisture *pro rata* than the ordinary copper corrosion product, the facts would be explained. So long, however, as this secondary product forms an inappreciable part of the total corrosion product, it is probable that the critical humidities for the two varieties will be essentially the same.

My second point refers to the evaluation of the results. The corrosion is measured by very delicate determinations of the weight-increment. It is clear that the weight increments of different metals may not be strictly comparable, since their chemical equivalents may vary.[7] Extending the argument, weight increments for the same metal but obtained under different conditions will only be comparable when the same corrosion product is formed in each case. Dr. Vernon has already shown (p. 265) that the composition of the copper corrosion product is affected by the concentration of the sulphur dioxide in the atmosphere ; the composition is probably also affected to an even greater degree by variations in the humidity, more particularly perhaps in the case of other metals than copper. I would, therefore, suggest that, if feasible, future results should be converted into values for the weight of metal corroded by means of the appropriate factors deduced from analyses of the final corrosion products. This should give a more absolute indication of the effects of variations in the factors considered on corrosion velocity.

Mr. J. H. Coste (*London*) said : This paper is extremely interesting as complementary to Dr. Vernon's previous (Inst. of Metals) paper on corrosion of copper in natural atmospheres. One small criticism which I have already made privately to the author is that, after taking so much care in saturating or knowing the percentage of saturation of the air entering the bell jar, it might have been advisable to make sure that in evacuating before introducing the desired atmosphere no uncertainty was caused by the probable disturbance of the hygroscopic state of the walls of the vessel,

which must have presented a considerable area. The use of a dew point hygrometer, of the type introduced by Regnault and much used latterly by Ezer Griffiths would have enabled the actual state of humidity within the vessel to be examined without being disturbed. The use of this form of hygrometer for determining the vapour tension of solutions was described in Findlay's " Practical Physical Chemistry" and seems to have first been described by A. C. Cumming[8] in 1909.

As to the actual results it is not clear whether the increment of weight in curve A (p. 261), is due in part to adsorbed air on the copper plate which had been exposed before the preliminary weighing to a vacuum overnight or whether this procedure had also been followed after exposure. The values on curve B might also be partly due to adsorbed water.

The atmospheres used were all much richer in SO_2 than, fortunately, are found, except perhaps near volcanoes, in nature. The SO_2 in London air varied from less than 0·00001 to about 0·0001 in a fog. The author's earlier paper showed that in these conditions a basic copper sulphate was formed and the present work confirms this for concentrations up to probably 1 per cent. The actual external atmospheric corrosion is complicated by the leaching effect of rain, which, in addition to sulphates, contains up to nearly 1 part per 100,000 of chlorions. In London, rain is usually acid only in winter, in summer the amount of alkaline dust from mortar and limestone is apparently enough to neutralise the sulphur acids brought down and collected with rain in the gauges used to measure atmospheric pollution.

As to the small effect of carbon dioxide in inducing corrosion and the rarity of the occurrence on corroded copper surfaces, an experiment carried out for me by my son P. R. Coste in which a bright copper disc was exposed for four months in a bell jar with a vessel containing sodium bicarbonate and water, without change of appearance or gain in weight being observed, affords confirmation of the insignificance of carbonic dioxide as a corrosion factor except, possibly, for very long periods of exposure and in an atmosphere where there is no more potent agent. Such an atmosphere, free from sulphur gases and chlorions could probably only be found in central Australia; the other continents are too industrialised.

Dr. Vernon, in reply, wrote : Dr. Hutton's suggestion that the different behaviour of emeried and sand-blasted specimens is due to differences in the state of oxidation of the surface is an interesting one. It must be remembered, however, that the phenomenon is exhibited only toward atmospheres containing sulphur dioxide. When the attack is due to the presence of hydrogen sulphide the difference in behaviour reduces to very small dimensions, no greater, indeed, than would be expected from consideration of the effective surface areas of the specimens. Yet it is with respect to attack by atmospheres containing hydrogen sulphide that the protective effect of invisible oxide films has been particularly established. It must be concluded, therefore, that the effects observed are not due to the presence of an invisible oxide film; to produce a film of sufficient thickness either a higher temperature or a much more prolonged exposure at ordinary temperature would be necessary. I take this opportunity to explain that the specimens employed in the investigations have always received a preliminary polishing with emery paper of the final (fine) grade shortly before every experiment. Time has then been given for the specimen to assume room temperature, when it has been treated extremely

[8] *J. Chem. Soc. T.*, 1772, 1909.

gently with the same emery paper, immediately prior to immersion in pure carbon tetrachloride (for de-greasing), followed by vacuum desiccation.

Dr. Patterson's reference to his contemporary work on the critical humidity phenomenon as it affects the rusting of iron is most opportune. His hypothesis, which associates the observed effects with the colloidal properties of the rust, is of great interest; to some extent it is the converse of the findings of the present paper, which indicate that, in the case of copper in the atmospheres investigated, critical humidity is determined by the hygroscopicity of the primary corrosion product. On the one hand the mechanism suggested is essentially physical, on the other hand, essentially chemical. I fully agree with Dr. Patterson that the mechanism that he has postulated for iron may apply (with varying incidence) to other metals also. If, however, it be assumed to find its extreme application in the case of iron, that may well explain the extraordinary extent to which the critical humidity phenomenon is displayed by that metal.

Mr. Evans emphasises the distinctions to be drawn between the behaviour of copper and the behaviour of iron. I am in complete agreement that, so far as atmospheric corrosion is concerned, iron must be considered as falling in a different category from that of copper. The available evidence goes to show that, on almost every count, the one metal supplies the antithesis to the other.

Dr. Lee has raised the interesting question whether a protective film can form continuously over a rough surface. The evidence of the sand-blasted specimens suggests that the answer is in the affirmative; for under the microscope the surface presents many facets, showing that, in these places the configuration is definitely angular. Yet in the hydrogen sulphide atmosphere the whole surface must become covered with a film of reaction product, which must remain unbroken; otherwise its near approach to the behaviour of the relatively smooth surface could not be maintained.

Dr. Martin states that I have brought forward no evidence for the existence of a catalytic action whereby copper sulphate is produced by the oxidation of SO_2 to SO_3 at the metal surface. I would reply that whereas there is definite evidence in support of this view, Dr. Martin has brought forward no evidence to the contrary. Certainly the work of Constable has no bearing upon the matter because that investigator was dealing with an entirely different reaction, namely the decomposition of ethyl alcohol into acetaldehyde and hydrogen; the activity of copper toward this particular reaction was studied from the point of view of developing the reaction-centre theory of catalysis. (Constable himself was careful to point out that " it is necessary to guard against its application to chemical reactions under conditions in which the continued existence of active spots would be impossible.") Dr. Martin says that " surely sulphur dioxide dissolves in an adsorbed film of water to form H_2SO_3 which is oxidised by aerial oxygen to H_2SO_4." But it is well known that whereas solutions of sulphurous acid undergo negligible oxidation·on exposure to air (low results in titration being due almost entirely to evaporation of SO_2), sulphite solutions on the other hand readily undergo oxidation. That catalytic activity may play a part even in the oxidation of sulphite solutions is recognised by Dr. Martin when he quotes the observation of Titoff concerning the influence of traces of copper sulphate. But this can scarcely be held to provide any support for Dr. Martin's view that the oxidation of sulphurous to sulphuric acid at the metal surface precedes the formation of copper sulphate. There are, in fact, a number of objections against this view. It is, for example, quite incompatible with the evidence of the present paper. The action of

dilute sulphuric acid upon copper is far too slow to account for the quantities of sulphate produced in the experiments. At the most, there must obviously be a considerable lag between the formation of sulphuric acid and the formation of copper sulphate, so that, on Dr. Martin's hypothesis, there must always be excess of sulphuric acid in association with copper sulphate. Actually there is never excess of sulphuric acid (on the contrary there is always excess of copper hydroxide) so long as the critical concentration of sulphur dioxide is not exceeded.

On Dr. Martin's hypothesis, moreover, sulphuric acid should be formed, under the conditions of the experiments, on surfaces other than copper. We have determined by experiment, however, employing exactly the same technique as in a corrosion experiment, that not even a trace of sulphuric acid is formed upon a glass surface (actually a glass crystallising basin was employed), under conditions such that a relatively large amount of sulphate would be formed upon copper. The experiment was repeated with the surface of the glass covered with the highly polar substance stearic acid, so that the most favourable opportunity was presented for the reaction postulated by Dr. Martin. In this case a definite film of moisture was observed upon the surfaces, in which, no doubt, sulphur dioxide dissolved freely; yet, again, no trace of sulphuric acid was found. The same negative result was obtained with a palladium-gold alloy (employed as a substitute for platinum which was not readily available).* Dr. Martin's hypothesis being clearly untenable, it seems most probable, therefore, that in the experiments described in the paper, copper does enter into the primary reaction, catalytically oxidising SO_2 to SO_3 with the formation of copper sulphate, as originally suggested.

The alternative explanation which Dr. Martin favours for the critical humidity phenomenon is essentially the same as that proposed by Dr. Patterson and Mr. Hebbs in their paper which was published together with my own, except that these authors were concerned only with the rusting of iron. I have already expressed the view that this physical mechanism need not be regarded as exclusive to iron, although possibly its incidence is at a maximum in the case of that metal and at a minimum in the case of copper. Nevertheless, I am indebted to Dr. Martin for the suggestion that it may play an important part in the much greater attack upon sandblasted specimens, and this suggestion is certainly worthy of further consideration.

In reply to Dr. Hudson I should explain that tables were omitted from the paper, with the object of saving space, in all cases where the results are plotted as curves. Nevertheless, I agree that if the precise numerical values are required, it is difficult to obtain these from the curves. In order to meet Dr. Hudson's point I have incorporated a collection of typical data in the accompanying table. It is difficult, in a reasonably compact table, to reproduce the whole of the values obtained in duplicate experiments, since the periods at which weight-increments were determined are not necessarily identical. The table is based upon the most usual periods, and duplicate values are given in all cases where the same period is common to the two experiments. In my view, however, what is of much greater importance than the agreement of two values at the end of a given period is the agreement of the two curves over the whole period; and for this reason I am unrepentant about having attached greater weight to the actual curves than to isolated values.

* The experiments were continued for 3, 8 and 4 days respectively.

TABLE III.—WEIGHT INCREMENTS OF SPECIMENS. MILLIGRAMS.

(To convert to mgms. per sq. dm., as plotted in curves, values should be doubled).

Atmosphere.	Period of Exposure. Days.								"Final" (Equilibrium) Values. (Plotted in Figs. 4 and 11.)
	1.	4.	7.	11.	15.	20.	25.	30.	
50 % R.H.									
0·01 % SO₂	0·036	0·062	0·072	0·076	0·091	0·094		0·087	0·092
0·10	0·037	0·088	0·121	0·157	0·127	0·131	0·177		} 0·135
	0·040	0·091	0·128	0·133	0·112	0·144	0·140	0·130	
0·50	0·086	0·176	0·234	0·263	0·279	0·265	0·277	0·295	} 0·285
	0·063	0·176	0·250	0·285	0·261				
1·0			0·140	0·155	0·160		0·160		} 0·160
	0·082	0·133	0·148						
2·0	0·111	0·249	0·245	0·280	0·319	0·346		0·348	} 0·350
	0·114	0·254	0·271	0·275	0·304				
10·0	0·274	0·566	0·687	0·733	0·711	0·755	0·774	0·806	} 0·790
	0·280	0·547	0·689	0·735	0·743	0·739	0·762	0·781	
75 % R.H.									
0·01 % SO₂	0·056	0·212	0·289	0·313	0·436	0·438		(0·480)	0·46
0·10	0·440	1·34	1·69	2·02	2·35	2·61			} 2·90
	0·413		1·70		2·43	2·68			
0·50	0·795	1·94	2·43	3·10	2·99		3·54		} 4·10
				3·13	3·33		3·68		
1·0			(0·435)			(0·755)			} 0·85
	(0·44)		(0·44)	(0·76)	0·80	(0·76)	0·90		
2·0	1·08	3·85	5·93	7·57	8·12		9·64		9·70
10·0	4·63	11·62	20·89	28·72	30·87	33·85			} 40·0
	4·38	11·07	21·10	28·23		33·59			
99 % R.H.									
0·01 % SO₂	0·497	0·843	1·02		1·53	1·67	(1·85)	1·96	} 1·85
	0·481	0·790	1·09		1·53	1·61	1·74	1·98	
0·10	5·79	6·48	6·93		6·97	7·14	7·43		} 7·50
	4·77	6·12							
0·50		2·50	4·36	5·86	7·24	8·49			} 10·6
	1·68	4·43	5·57	6·49	7·09	8·57			
1·0	2·42	2·85	2·70	3·27	3·67	3·43	4·11		} 4·20
	2·38	2·73	2·88	3·37	3·43	3·55	4·16		
2·0	5·43	8·51	9·76	10·96					} 13·2
	5·87	8·44	10·08	10·19		12·57		13·16	
10·0	26·51	37·28	40·66	41·87	41·50	45·85		46·65	} 44·0
	26·50	37·89	39·89	40·87		43·19		44·92	

I am indebted to Dr. Hudson for pointing out a possible source of confusion between the values for critical humidity as published in the present paper and those found in his previous work as the result of experiments in which the corrosion product was submitted to increasing relative humidities. Dr. Hudson's work showed clearly that the common metals vary greatly in the readiness with which their products exhibit visible condensation of moisture upon the surface; and in this respect copper

occupied an extremely favourable position.   That observation is confirmed by the results of the present paper, because, except at the highest concentration of sulphur dioxide at the highest relative humidities, there has been a remarable freedom from visible moisture upon the specimens.   The term critical humidity is used in the paper in the rather more fundamental sense of denoting that humidity below which the *actual attack upon the metal* is negligibly small and above which it may become extremely marked.

I agree with Dr. Hudson in his interpretation of the behaviour of corrosion products from H.C. and arsenical copper respectively.   There is no need to assume that the critical humidity (as measured in terms of relative humidity) is different in the two cases ; but the effects produced (in terms of water taken up) are greater upon H.C. than upon arsenical copper.

Dr. Hudson's final point is to some extent a " counsel of perfection." I quite agree with the desirability of expressing all values in terms of actual metal attacked.   We have perforce, however, to adopt the weight-increment method as affording the most satisfactory method of following the changes taking place at the surface.   As Dr. Hudson observes, to convert weight-increment into terms of metal attacked involves a knowledge of the chemical composition of the product.   But we have shown that this varies with every change in the composition of sulphur dioxide in the atmosphere ; accurate information as to the nature of the relationship was, indeed, only obtained when the work was far advanced.   The conversion of all values, in the light of our final knowledge, would be somewhat involved, but the general disposition of the curves would not be affected ; neither of course would be the actual values of the critical points in terms of concentration of sulphur dioxide.   In order to get some idea of the values concerned, it may be noted that in Fig. 11 the peak position in the curve for 99 per cent. RH at 0·5 per cent. SO_3 corresponds with a weight of metal attacked of 12·9 mg. per sq. dm. (*cf.* weight-increment of 21·2 mg. per sq. dm.) and the minimum point at 1·0 per cent. SO_2 with a weight of metal attacked of 5·15 mg. per sq. dm. (*cf.* weight-increment of 8·4 mg. per sq. dm.).

Mr. Coste has suggested the possibility of disturbances in the hygrometric conditions being brought about by moisture films on the walls of the bell-jar.   I do not think, however, that any appreciable error can arise from this cause.   Certainly there is no evidence of any visible condensation of moisture, so that we have, therefore, to consider only invisible, adsorbed films.   But the evacuation of the bell-jar previous to filling would not be nearly sufficient to remove any such adsorbed film; and it is highly probable that the state of the surface in this respect is uniform from one experiment to another.   In any case, any variation must be of a far lower order of magnitude than would be necessary to affect appreciably the relative humidity of the atmosphere entering the bell-jar.

I agree with Mr. Coste that the weight-increments plotted in curve A (p. 261) must include the weight of adsorbed films upon the metal, in addition to the "genuine" weight-increment due to reaction with oxygen ; and I agree also that curve B must be afflicted with the same error.   The point is, however, that any such error must be definitely smaller in magnitude than the values plotted in curve A, and, hence, of negligible proportions as compared with values plotted in other curves.

Mr. Coste raises an important point when he states that the concentrations of sulphur dioxide employed in the experiments are greatly in excess of the amount normally present in the atmosphere.   This is true even of

the lowest concentration employed, *i.e.*, 0·01 per cent. or 1 volume in 10,000. Nevertheless, we have followed a procedure that is perfectly justifiable. Previous work has shown that the major constituent of the corrosion product of copper in the open is basic copper sulphate, which must be derived from the action of sulphur dioxide in the atmosphere. Increasing greatly the concentration of sulphur dioxide has enabled us to obtain results within a reasonably short space of time; this procedure, however, has not introduced an entirely new factor, it has merely intensified a factor known to be present in service conditions. Admittedly, the higher concentration of sulphur dioxide were employed merely to amplify information which had emerged from experiments with the lower concentrations; nevertheless, it is possible that even these results may have some intrinsic interest. In the aggregate, the results have enabled us to survey the field as a whole and to identify three ranges, one of which corresponds to the range within which the green patina of basic copper sulphate may be formed in practice.

The experiment carried out by Mr. P. R. Coste is of very great interest, as confirming the (virtually) negligible effect of atmospheric carbon dioxide upon copper, and I am much indebted to Mr. Coste for having included a reference to this experiment in the present discussion.

THE RELATION OF THE MOISTURE IN RUST TO THE CRITICAL CORROSION HUMIDITY. *

DISCUSSION.

(At a meeting of the Faraday Society held on 10*th June*, 1931.)

Dr. W. H. J. Vernon said : I am glad that this interesting paper by Dr. Patterson and Mr. Hebbs appears together with my own[1] because it bears opportunely upon a related and important part of the subject. The authors deal with critical humidity as it affects the corrosion of iron ; my own paper deals with critical humidity as it affects the corrosion of copper. The results are similar, yet the mechanism would seem to be different.

In the case of copper exposed to an atmosphere containing sulphur dioxide, the critical humidity phenomenon is definitely associated with the chemical hygroscopicity of the product. We have been able, indeed, to obtain a direct correlation between the behaviour of the product when separated from the metal and the behaviour of the actual specimen with the corrosion product *in situ*. On the other hand, the authors' results would suggest that no such correlation obtains in the case of iron. Yet the phenomenon itself is most striking and is undoubtedly of fundamental importance. Clearly, we have to consider, not so much the properties of the rust *per se*, as the properties of a system in which rust and iron are contiguous. The authors are to be congratulated upon having put forward an hypothesis which must certainly be taken into account in any further work on the subject. For the moment, the point that I wish to emphasise is that whereas the mechanism postulated by the authors for iron is essentially physical, depending upon the colloidal properties of the rust, in the case of copper it is essentially chemical, depending upon the chemical

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* See this vol., p. 277.   [1] This vol., p. 255.

properties of the initially-formed product. It is not necessary, of course, to assume that these two types will be mutually exclusive; intermediate cases may naturally be expected.

Dr. W. S. Patterson, in reply, said: I quite agree with Dr. Vernon that there is a pronounced difference between the corrosion of iron and that of copper. Dr. Vernon has himself shown that the corrosion products on copper are continuous whilst those on iron are definitely discontinuous or porous. In the former case chemical changes in the scale would be the principal way in which the corrosion could be modified, whilst in the latter the effect of capillaries in the porous scale would be likely to be of importance. It is hoped to investigate the corrosion products formed on zinc by a similar method with a view to elucidating whether or not the colloidal properties of zinc hydroxide play a part in the atmospheric corrosion of zinc in unsaturated atmospheres.

THE COLLOID THEORY OF THE CORROSION OF IRON AND STEEL.

By J. Newton Friend.

(Presented at a meeting of the Faraday Society held on 10th June, 1931.)

Ten years ago [1] I had occasion to direct attention to the close similarity between the phenomena attending the corrosion of iron—using the word iron in its broadest chemical sense to include steels and ferrous metals generally—and the formation and precipitation of colloids. This similarity was too striking to be merely accidental, and later research has fully confirmed the observations then made.

In the same paper I showed that if ordinary tap water is made to flow over the surface of iron, the rate of corrosion rapidly increases with the velocity of the water, a maximum effect being reached at a speed of about 0·1 mile per hour. Further increase in the rate of flow of the water resulted in a decrease in the rate of corrosion, until, at a velocity of about 6 miles per hour no corrosion in the ordinary sense of the term will take place. It is true that a slight loss in weight occurs, but this is probably due in the main to mechanical erosion. The experiment may be varied by first rendering the water milky with bubbles of air, but the result is the same, showing that lack of oxygen is not the cause of the freedom from rusting.

In order to ascertain whether or not the same kind of retardation would occur under conditions of rapid movement in acid solutions discs of pure iron foil were made to rotate at varying speeds in glass tanks containing dilute sulphuric acid.[2] It is admitted that the two sets of experiments were not strictly comparable. In the tap water tests the water flowed over the iron contained in a glass tube and ran to waste so that the same water never passed over the metal a second time. To have adopted the same method with acid would have required enormous supplies of acid, and this was impracticable. Nevertheless the results obtained were very instructive, for it was found that, within the error

[1] Friend, *Trans. Chem. Soc.*, 119, 932, 1921.
[2] Friend and Dennett, *ibid.*, 121, 41, 1922.

of experiment, the rate of solution of the iron was directly proportional to the velocity of rotation. At 4000 revolutions per minute, corresponding to a velocity at the rim of the disc of some 35 miles per hour, there was no sign of falling off in the rate of solution. Whitman and his co-workers [3] have confirmed and extended these results.

The conclusion was inevitable that a great difference exists between corrosion in more or less neutral solution and corrosion which is the result of acid attack, in which the products of corrosion are soluble and readily wash or diffuse away from the seat of attack. I was therefore led to suggest a new theory of corrosion according to which iron is relatively noble or passive to pure ærated water, and only passes into solution with extreme slowness in the absence of a catalyst. The dissolved iron is probably present at first in solution in the more or less completely ionised condition, and it was suggested that agglomeration of ferrous hydroxide then took place, the colloid thus formed catalytically assisting the as yet unattacked metal to undergo corrosion.

At first the *modus operandi* of the colloid was assumed to be chemical, the ferrous hydroxide functioning as an oxygen carrier being alternately oxidised by dissolved oxygen and reduced by the metallic iron.

Such a series of reactions is theoretically possible, and harmonises with the well-known catalytic activity of iron and its salts in numerous reactions. But a series of carefully planned experiments carried out with the object of testing this theory have yielded negative results. Whilst, therefore, the foregoing scheme is still possible, it seems more likely that the action of the colloid is simply mechanical. That is to say, in rapidly moving aerated water the iron passes very slowly into solution and the ferrous hydroxide is swept away. Under stationary or slow-moving conditions the iron passes into solution as before, but the ferrous hydroxide agglomerates to sol or gel and is adsorbed on to, or otherwise clings to, portions of the metallic surface, thus partially screening them from oxygen and inducing anodic corrosion in accordance with recognised electrochemical principles.

The corrosion of iron under such conditions, therefore, is largely interwoven with colloid phenomena, for it is evident that any reaction or process that will retard adsorption and the consequent screening of the metal surface will tend also to retard anodic attack.

DISCUSSION.

Mr. U. R. Evans (*Cambridge*) said: Dr. Friend's paper is extremely welcome, as an expression of opinion which should gain wide acceptance. The application of colloid-science to corrosion by Dr. Friend has shown two features: (1) his demonstration of the surprising extent to which *organic colloids* are capable of retarding corrosion reactions, and (2) his views on the part played by *colloidal iron hydroxides*. It is a matter for regret that, owing to the heat of the controversy which arose over the second feature of Dr. Friend's earlier papers on these matters, the importance attaching to the first feature has been somewhat overlooked, and the thanks due to Dr. Friend for these discoveries have never been fully expressed. Perhaps it is not too late to make amends.

[3] Whitman and co-workers, *Ind. Eng. Chron.*, **15**, 672, 1923 ; **17**, 348, 1925.

THE CALCULATION OF THE EQUIVALENT CONDUCTANCE OF STRONG ELECTROLYTES AT INFINITE DILUTION. A REPLY TO SOME RECENT CRITICISM.[1]

DISCUSSION.

Dr. C. W. Davies[2] (*London*) wrote :—

Drs. Ferguson and Vogel quote a comment of mine : "Ferguson and Vogel's method of calculation has the disadvantage that the actual experimental figures cannot be used ; conductivity values at suitable concentration intervals must first be read off from a smoothed curve. In using such a method the weight consciously or unconsciously assigned to each point in drawing the first curve is reflected in the result of the second, so that the process as a whole is not reproducible in the hands of different workers." They say : "We find it difficult to attach any meaning to this sentence."

My meaning is illustrated by the figures Drs. Ferguson and Vogel cite. Parker's data for HCl at $25°$ yielded[3] the value $n = 0.96716$ when the interpolated values of Parker were used, and a value "lying between 0.5 and 0.6" when the interpolation was carried out by the authors themselves. For five series of measurements on KCl at $18°$ I obtained the values $n = 0.64, 0.66, 0.51, 0.44$, and 0.39, while Ferguson and Vogel reject two series and find for the others $n = 0.587$ and 0.585. It is true that in obtaining my results I did not strictly follow Ferguson and Vogel's directions, but I used a method which should lead to the same results, and does so— as the authors agree—for hydrochloric acid.

Drs. Ferguson and Vogel also take exception to my statement : "n cannot be determined within narrow limits. Ferguson and Vogel's value for KCl, $n = 0.4520$, is obviously not incompatible with the square root rule." In view of the numbers just quoted, this statement needs no further justification. Using Kohlrausch's data Ferguson and Vogel put forward the value : $n = 0.4520$; from Weiland's figures they now find $n = 0.586$. The mean is 0.519.

Finally, Drs. Ferguson and Vogel quote my comments, that they "reject Kohlrausch's square root rule," and that their "results are directly opposed to the theory of Debye and Huckel." They regard these remarks as startling misinterpretations, and I should therefore be allowed to explain that they were based on sentences such as the following :[4]

"The assumption of the constancy of n is fundamental in certain new theories of strong electrolytes. Debye and Huckel, for instance, find that their theory leads directly to Kohlrausch's square root formula ("Gesetz")

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = Bc^{\frac{1}{2}},$$

where B is determined in terms of certain constants for the substances concerned and the exponent of c is independent of the nature of the electrolyte. This is directly opposed to the results we have obtained."

Dr. A. R. Martin[5] wrote : First let me deal with the comparatively minor point of testing the fit of the equation $\Lambda_0 = \Lambda + Bc^n$ by comparing the consistency of the values of Λ_0 calculated from it with that of those

calculated from the square root law, using in both cases rounded values of Λ read off from the plot of Λ against c used in determining the constants B and n. It is true that this procedure tests the exactitude with which the curve drawn with the flexible spline conforms with the equation $\Lambda_0 = \Lambda + Bc^n$, as Drs. Ferguson and Vogel admit—"What the equation to the curve will turn out to be is a matter for further investigation—it may, or it may not, be represented by $y = a + bx^n$. That is the point which is tested by the process." However, the experimental points lie distributed more or less evenly on both sides of the curve : and in order to test the exactitude with which *they* are represented by the equation $\Lambda_0 = \Lambda + Bc^n$ it would be necessary to substitute the actual experimental data, not the rounded values, in the equation, and to find the constancy of the values of Λ_0 so calculated. I wonder if Drs. Ferguson and Vogel would admit the legitimacy of the procedure, strictly analogous to theirs, of testing the accuracy with which the square root law is obeyed by plotting Λ against $\sqrt{c}$, drawing a straight line through the points (which in the majority of cases of strong electrolytes can be drawn at least as unequivocally as the Λ, c curve), substituting values of Λ read off from the straight line in the equation $\Lambda_0 = \Lambda + x\sqrt{c}$, and showing that consistent values of Λ_0 are obtained.

It appears to me that in many cases the very slightly superior fit of the equation $\Lambda_0 = \Lambda + Bc^n$ over the square root law is of roughly the order of magnitude of the accidental error of the conductivity measurements, quite apart from any systematic error which may be present.[6] The fact that n is not exactly 0.5 (but is, say, $0.5 \pm$ about 0.05) does not by itself tell greatly against the Debye-Hückel theory : a safer test is the slope of the Λ, $\sqrt{c}$ straight line. One is certainly not justified in quoting n to the fourth place of decimals as Drs. Ferguson and Vogel did in their earlier papers.

The best method of extrapolation is the square root law, provided the slope x in the equation $\Lambda_0 = \Lambda + x\sqrt{c}$ is that predicted by Onsager's modification of the Debye-Hückel theory. On the other hand, if x differs appreciably from the theoretical value, a purely empirical method such as that of Drs. Ferguson and Vogel is, if used with caution, preferable. Unfortunately in some cases in non-aqueous solution where x is very considerably greater than the theoretical value (for example, silver nitrate in benzonitrile) the equation $\Lambda_0 = \Lambda + Bc^n$ is not obeyed over a wide enough range to permit an accurate determination of the constants B and n, and, for lack of anything better the square root law must be used, although it is not obeyed over a wide range.[7] In such a case a variant of the trial and error method using the equation $\Lambda_0 = \Lambda + x\sqrt{c} + \dfrac{\Lambda_0 c}{K}$, where x is the theoretical Debye slope, might be useful if a very refined value of Λ_0 is desired. This suggestion is only to be regarded as provisional, since no calculations have been performed. It rests on the assumption that the sole cause of deviation from the Debye-Hückel-Onsager equation is incomplete dissociation. If it is desired to see if incomplete dissociation will account for this deviation, it is more convincing to extrapolate by a method which does not prejudice the issue.

[6] See Table I., *J. Chem. Soc.*, 3277, 1928.
[7] Compare Hartley, *Ann. Reports, Chem. Soc.*, 346, 1930.

Professor Alfred W. Porter, D.Sc., F.R.S., wrote :[8] To lead up to the question of the reliability of extrapolation I will examine a set of observations by way of illustration.

1. Let the following be the data obtained in a set of observations, x and y being the co-ordinates of a line :—

x.	y.
0·48496	0·85712
·47008	·84805
·45536	·83867
·44081	·82904
·42642	·81915

It is required to find the value of y when x is zero.

The data lie so nearly upon a straight line that we first choose a straight line $y = mx + c$ so as to lie amongst the given points. Either by plotting or by calculation it is found that $m = 0·64948$ gives a satisfactory slope to the line and with this value we calculate the values of c corresponding to each of the given values of x and y. These values of c are

$$0·54214, \quad 0·54274, \quad 0·54292, \quad 0·54274, \quad 0·54220$$

These values differ from their mean by less than 4 parts in 10,000. I understand that Dr. Ferguson would claim that this close concordance would justify us in deciding that this mean value (*viz.* 0·54255) is a safe value to take for the zero ordinate of the curve through the given points.

In reality, however, the close concordance indicates merely that the data lie close to a straight line and gives no indication as to the value of the zero ordinate. This conclusion follows at once from the fact that to calculate c from the data and a *constant* value of m is equivalent to drawing *parallel* lines through the data and finding the points where these lines cut the y-axis. The separation of these lines at $x = 0$ is therefore necessarily exactly the same as their separation within the range of the data themselves.

ii. A closer inspection of the data would show that a better fit can be obtained if we assume a curved instead of a straight line. In the case of experimental data it might be difficult or even impossible to decide this because of the accidental (*i.e.* irregular) errors to which such values are subject. It is usually still more difficult to decide on the nature of the curvature, *i.e.* as to whether it is constant, increasing or decreasing with x. Widely different values may be obtained for the zero ordinate in the various cases. In the case of the data given above the decision is much easier because they have been obtained from trigonometrical tables and represent points lying exactly (*i.e.* to the fifth significant figure) on a *circle which passes through the origin !* The correct extrapolated value is thence zero instead of 0·54255.

Obviously, then, some additional test is necessary before a safe extrapolation can be made. Without attempting in this place to give a general theory it may be pointed out that a suitable test in the case of the above data is to take differences of successive y's and differences of successive x's and find their respective ratios.

Δy.	Δx.	$\Delta y/\Delta x$.	Differences.
0·00907	0·01488	0·6108	
			0·026
·00938	·01472	0·637	
			·025
·00963	·01455	0·662	
			·025
·00989	·01439	0·687	

The ratios in the third column should all be the same if the curve (y, x) is a straight line; but there is a progressive change in value indicating the existence of curvature.

iii. Now in Dr. Ferguson's problem the assumption is made that the equation for λ in terms of C is $\lambda = \lambda_0 - bC^n$ where b and n are constants. Taking the observed values of λ for concentrations in geometric progression (ratio R) and subtracting neighbouring values he obtains

$$\varDelta_p = b(C_{p+1}^n - C_p^n) = bC_p^n(R^n - 1)$$

or $\qquad \log \varDelta_p = \log\{b(R^n - 1)\} + n \log C.$

If his assumption is right this will be a straight line on a logarithmic diagram and by drawing a mean straight line fitting the points as nearly as possible he can determine the values of b and n. If now, using these values, the values of $\log (\lambda_0 - \lambda)$ are calculated and thence the values of λ_0, these differ somewhat from one another; and because these differences are small he considers that he is justified in relying upon his values for b and n. But, as in the analogous case in section i. the smallness of the differences merely shows that the straight line fits fairly at *interpolated* points.

Some additional criterion is necessary as in section i. Let us try the criterion afforded by successive differences.

$\delta \log C.$	$\delta_1 \log \varDelta.$	$\delta_2 \log \varDelta.$	$\delta_3(\log \varDelta).$
·3010	− ·20412		
		·0465	
·3010	− ·15761		·0185
		·0280	
·3010	− ·12963		·0198
		·0082	
·3010	− ·12143		·0196
		− ·0114	
·3010	− ·13281		

The differences in $\log \varDelta$ for equal differences in $\log C$ should all be equal; in point of fact they vary considerably. Even third order differences have to be made to obtain approximate steadiness. This test is decidedly unfavourable to the linearity of the equation for $\log \varDelta$ against $\log C$.

iv. Taking the result of this test in connection with the Kohlrausch-Debye square-root law which has serious theoretical support as being a first approximation I have fitted a four-term expansion

$$\lambda = \lambda_0 + b \sqrt{C} + gC + hC^{3/2}$$

to Kohlrausch's values for KCl, the values of the constants being calculated from the data for concentrations

$$1, 4, 16, 64 \times 10^{-4} \frac{\text{gr. eq.}}{\text{litre}}.$$

The result is

$$\lambda = 129\cdot80 - \cdot703\ C^{\frac{1}{2}} - \cdot0342\ C + \cdot0035\ C^{3/2}$$

the unit of concentration being 10^{-4} gr. eq./litre. This, of course, fits exactly at the four strengths chosen which cover the whole range of experimental values. The contributions of the several terms at the strongest concentration are

$$128\cdot78 = 129\cdot80 - 5\cdot62 - 2\cdot19 + 1\cdot79.$$

This is still convergent but it is not converging fast, and it is clear that additional terms would be necessary to obtain λ correct in the unit place. So it is not encouraging.

v. Lastly, it is well to see what sort of success can be obtained with the square-root formula,

$$\lambda = \lambda_0 + b\ \sqrt{C.}$$

Taking $b = -\ 0\cdot757$ the following values of λ_0 are obtained :—

C.	λ_0.
1	129·83 ⎫
2	129·87 ⎪
4	129·80 ⎪
8	129·80 ⎬ Mean λ_0 = 129·81.
16	129·70 ⎪
32	129·84 ⎪
64	129·83 ⎭

There is no simple law of progression for these values. It must be concluded that the *experimental* errors are of the same order as the fluctuations from the mean. A direct plot of the experimental values shows also that the last place is certainly not to be trusted. If this is so then the simple Debye formula holds as well as any to represent a smoothed curve drawn through the experimental values, which are not sufficiently accurate even in the case of KCl to justify further elaboration.

THE THERMAL DISSOCIATION OF AMMONIA ON TUNGSTEN.

By H. R. HAILES.

The decomposition of ammonia on the surface of tungsten has been investigated by Hinshelwood and Burk,[1] Kunsman,[2] and Schwab.[3] All of these workers conclude that at high pressures the reaction is almost zero order. This provides an indication that the active surface of the tungsten is nearly saturated with ammonia gas. At pressures in the neighbourhood of 2 to 26·5 cm., Kunsman finds that the reaction tends to become unimolecular as the concentrations in the gas phase diminish. He also finds that excess of nitrogen and hydrogen, particularly the latter, exerts a retarding effect on the rate of reaction. Schwab,

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[1] *J. Chem. Soc.*, **127**, 1105, 1925.   [2] *J.A.C.S.*, **50**, 2100, 1928.
[3] *Z. physik. Chem.*, **128**, 161, 1927.

working at pressures in the neighbourhood of 10^{-2} cm. also finds very great retarding effects on the reaction by nitrogen and hydrogen. He also notes a retarding effect by argon.

The critical increment of this reaction was found by Hinshelwood and Burk to be 38,700 cal. between 900° to 1100° A., and Kunsman came to the conclusion that the increment varied between 35,000 cal. at 1000° to 1250° and 45,000 cal. at 800° to 1000° C.

This reaction has been studied in the present investigation for two pressures of ammonia, viz., 3·7 cm. and 0·7 cm. and at temperatures of the tungsten filament ranging from 950° to 1150° A. The pressure of ammonia was kept constant throughout the reaction at any one temperature. Thus, the effects of the products on the reaction rate could be determined at a constant pressure of ammonia. At the above constant pressures of ammonia, there was observed no retardation of the rate of reaction by the products. The values of the critical increment seem to vary with the pressure. The results so far obtained for the critical increment of this reaction are given in Table I.

TABLE I.

900°-1100° A. Pressure.	Critical Increment.
50-100 mm.	38,700 cal. (Hinshelwood and Burk).
100 mm.	45,000 ,, (Kunsman).
37 ,,	31,060 ,, ⎫ (Hailes).
7 ,,	26,800 ,, ⎭

The observed decrease in the critical increment between 100 mm. and 7 mm. could be accounted for in the case of a zero order reaction if the products retard the heterogeneous reaction, but the present experiments definitely rule out this possibility.

In the case of a reaction which is not exactly zero order, and for which there is no retardation by the products, it is possible to explain the decrease in the critical increment in another way. The observed critical increment is related to the critical increment of the molecules in the gaseous phase by the relation $E_0 = E_g - Q_A$, where Q_A is the heat of adsorption.[4] This equation will hold provided the rate of adsorption is much more rapid than the rate of chemical change, that is to say, that the adsorption attains its equilibrium value during all the stages of the reaction. The heat of adsorption, Q_A, increases as the degree of saturation of the surface decreases;[5] therefore E_0 should be reduced if the surface of the tungsten becomes less saturated with ammonia. The actual decrease in E_0 is 20,000 cal., and this is well within the limits of the changes in Q_A found experimentally. In the case of the decomposition of ammonia on tungsten, it is clear that the degree of saturation of the surface with ammonia varies with pressure. This must be the case, since the rate of reaction at constant temperature decreases with fall in pressure. It is concluded, therefore, that the variation in the critical increment with pressure is due to changes in the heat of adsorption.

[4] Polanyi, *Z. Elektrochem.*, **27**, 143, 1921 ; Hinshelwood, *Kinetics of Chemical Change*, p. 232, 1929.
[5] *Cf.* Taylor, *J.A.C.S.*, **53**, 578, 1930, where a summary of heats of adsorption is given.

Theory of Polanyi and Wigner.—According to this theory,[6] the rate of the surface reaction is given by the equation :

$$- dx/dt = A \cdot n \cdot v \cdot d \cdot e^{-E_0/RT},$$

where A is the area of the surface, n is the number of molecules per c.c. of gas, d is the thickness of the adsorption space $= 10^{-8}$ cm. approximately, and E_0 is the observed critical increment. v is the frequency of vibration of the adsorbed molecule. At 969° A. and 3·621 cm. pressure, A being equal to 1·852 cm.[2], the observed rate of reaction is 9·766 × 10^{16} molecules per second. From the above equation, substituting the experimental values, $- dx/dt = 2\cdot432 \times 10^{11} \times v \cdot d = 9\cdot766 \times 10^{16}$. Therefore $v \cdot d \cdot = 4 \times 10^5$. Since $d = 10^{-8}$, it follows that $v = 4 \times 10^{13}$, which is of the right order. The calculated value for homogeneous reactions is usually found to lie between 10^{13} and 10^{14}.

The above theory assumes that adsorption equilibrium is rapidly established, and that the rate depends upon the rapidity with which adsorbed molecules can acquire activation energy from the surface. An alternative theory, which postulates that all those molecules undergo reaction which strike the surface with a critical energy $= E_0$, does not give satisfactory agreement with the observed rates. The number of molecules striking the filament per second, $N = 1\cdot848 \times 10^{22}$. Of these, $e^{-E_0/RT}$ will possess a critical energy of the correct magnitude. The rate of reaction should, therefore $= N \cdot e^{-E_0/RT} = 1\cdot882 \times 10^{15}$ molecules per second. The actual observed value is $9\cdot77 \times 10^{16}$.

These experiments therefore support the theory of Polanyi and Wigner.

Experimental.

Fig. 1 shows the essential features of the apparatus. The reaction
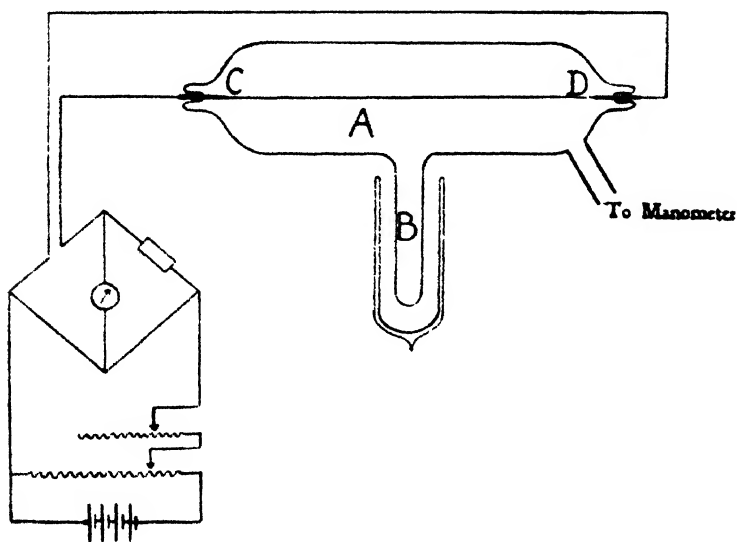
FIG. 1.

vessel (A), of capacity approximately 1 litre, was made of Pyrex glass

* Z. physik. Chem., 139, 439, 1928.

of diameter 6 cm. and length 35 cm.   The appendix (B) was of 1·5 cm. tubing and 15 cm. long.   The filament (CD) consisted of pure 0·18 mm. tungsten wire, spot welded by platinum on to thick tungsten leads and sealed into glass.   This was connected to a Wheatstone Bridge and its resistance determined.   The method adopted for keeping the filament at constant temperature was that used by Kunsman, and the temperature-resistance curve used for the filament was that due to Jones.[7] Owing to the high thermal conductivity of hydrogen, it was necessary to increase the current through the filament continuously during the course of an experiment.   The resistance of the wire was kept constant by balancing against a known resistance, using a Broca galvanometer as a zero instrument.

The ammonia was prepared from ·880 ammonia, and purified by fractional distillation from the liquid state.   It was dried over metallic sodium.

Before an experiment, ammonia was condensed in the appendix (B), and maintained at constant temperature by surrounding (B) with solid CO_2 and methylated spirits or by frozen toluene.   The toluene had been carefully purified before use.   The pressure of the ammonia in the reaction vessel was read off directly in a mercury manometer by means of a Wilson travelling microscope.   Readings were taken every five minutes during an experiment, and at the end of a series of measurements, the final reading was checked by condensing out the ammonia with liquid air.   In these experiments, the ammonia converted to hydrogen and nitrogen was replaced by the evaporation of the ammonia in appendix (B).

Results.

Table II. gives the experimental results for the two pressures investigated.
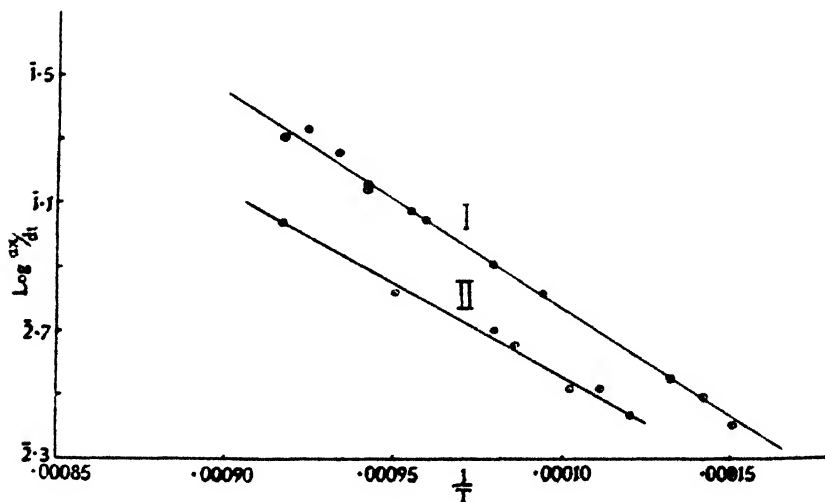
FIG. 2.

Column 2 gives the temperature of an experiment, 3 the velocity in cm./min., and 5 the pressure.   The last column records the value of the critical increment calculated from consecutive experiments.

[7] *Physical Rev.*, **28**, 202, 1926.

TABLE II.

No. of Expt.	Temp. °Abs.	dx/dt (cm. per min.).	Duration of Expt. (mins.).	Initial Press. (cms.).	E (cals.).
3	1090	0·200	18	3·625	
4	1062	0·138	45	3·550	29,570
5	1047	0·118	55	4·316	23,920
6	959·6	0·031	160	4·169	30,660
7	969·4	0·035	140	3·621	27,070
8	1006	0·066	120	3·558	32,380
9	1043	0·111	70	3·678	29,720
10	1062	0·143	60	4·036	27,050
11	1082	0·213	40	3·688	44,030
13	1022	0·080	100	2·726	29,910
14	1072	0·179	50	3·347	34,550
15	952·7	0·025	125	4·060	33,340
1	997·6	0·033	60	0·706	
3	1091	0·108	45	0·691	25,660
4	1053	0·066	45	0·711	25,320
5	1015	0·045	50	0·696	21,180
6	980·3	0·027	65	0·701	29,470
9	1021	0·050	60	0·863	30,210
10	988·9	0·033	60	0·750	26,200

These results are also plotted in Fig. 2, curves I. and II., and from these graphs, $E_{3·7\,cm.} = 31,055$ cal. and $E_{0·7\,cm.} = 26,800$ cal.

Effect of Products.

A few experiments were carried out with a limited supply of ammonia at a pressure 3·7 cm., and as in the case of the curves of Hinshelwood and Kunsman, the rate of reaction falls off with time. That this decline in the rate is not due to adsorption of the products on the tungsten wire is shown by experiments in which the pressure of the ammonia is kept constant. When the pressure of the ammonia is constant throughout an experiment, then the rate of reaction is also constant (see Fig. 3), even though the reaction is followed until the pressure within the system has been doubled. The retardation of the reaction by nitrogen and hydrogen observed by Kunsman is therefore most probably due to a decrease in the saturation of the surface with ammonia as the pressure falls.

Summary.

The rate of decomposition of ammonia on the surface of tungsten has been studied at the two pressures 3·7 and 0·7 cm., over a temperature range 950° to 1150° C. The ammonia pressure was kept constant during an experiment, and it was found that the products of the reaction did not retard the rate of decomposition.
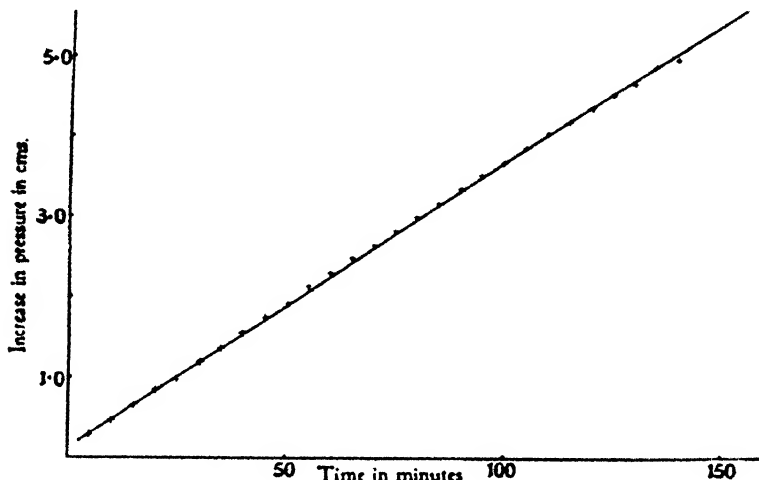
FIG. 3.

The critical increment was 31,060 cal. at 3·7 cm., decreasing to 26,800 cal. at 0·7 cm. pressure. This decrease is explained as due to an increase in the heat of adsorption of ammonia as the gas pressure is lowered. It is concluded that the surface of the tungsten is not saturated with ammonia at these pressures.

Calculations made from the rate of reaction agree with the theory of Polanyi and Wigner.

This research was carried out under the direction of Professor W. E. Garner, to whom the author's thanks are due for his constant interest and advice.

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THE EFFECT OF HYDROGEN-ION CONCENTRA-TION ON THE CORROSION OF TIN.

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Corrosion of tin-plate by fruit acids is a problem of no little importance to the canning industry. The subject is fully discussed in a special report [1] of the Department of Scientific and Industrial Research. Conditions which promote de-tinning are harmful, quite apart from any considerations

such as metallic contamination or possible discoloration of the food product. Any influences which encourage de-tinning of the container tend to cause the area of tin to decrease rapidly, with a corresponding increase in the area of exposed steel base; the latter metal, then being partially deprived of the protection of the tin, is subject to corrosion by the fruit acids. It is remarkable that the greatest losses through corrosion are experienced, not with fruits of high acidity, but with those of low acidity (p_H 3·5 to p_H 4·5 approximately). It was thought that a study of the factors which influence the corrosion of pure tin, especially the hydrogen-ion concentration, might throw light on this fact. This expectation has not been realised; in fact, in all of the experiments which follow tin suffered the most rapid attack at high acidity. As may be seen, however, from a study of the Report already mentioned the corrosion of tin-plate is affected by a large number of factors, such as the peculiar behaviour of tin and iron in couple and the presence of substances other than acids in the fruit juices or syrups. At the same time these studies on tin are of interest in themselves, and must ultimately be found to have some bearing on a general explanation of the corrosion of cans.

Historical.

Like other metals of low melting-point and little power of adsorbing hydrogen, tin has a high hydrogen-overvoltage. Consequently, although it falls below hydrogen in the electro-chemical series, it tends to behave like one of the more noble metals, and is not readily attacked by non-oxidising acids in the absence of oxygen. Numerous investigators [2-5] have shown that distilled water has little or no action on metallic tin, but some difference of opinion still exists as to whether the metal is wholly immune from corrosion. A large number of workers, notably Chapman,[6] De Fouw,[7] Lehmann,[8] and Hall,[9] report that tin is not attacked by dilute organic acids, such as citric and tartaric acids, to any appreciable extent in the absence of oxygen; when oxygen is present, however, the metal dissolves fairly readily. Experiments by Whitman and Russell [10] have demonstrated the accelerating influence of oxygen on the corrosion of tin by acids; they observed, however, that the effect of dissolved oxygen was overshadowed in the case of an oxidising acid, such as nitric acid. Watts and Whipple [11] found that the addition of oxidising agents to mineral acids caused a marked acceleration in corrosion, and a similar observation was made by Prins [12] in the case of substances that were readily reduced. The corrosive action of ferric chloride is well known, as it forms the basis of one of the commercial processes for the recovery of tin from scrap tin-plate. Van Name and Hill [13] measured the rate at which ferric salts reacted with tin and other metals in the presence of varying amounts of free acid, and their results show that the velocity of the reaction in normal cases is proportional to the concentration of the oxidising agent.

The principal factor which prevents tin from dissolving appears to be its high overvoltage and low power of catalysing the reaction $2H^+ = H_2$. Oxygen or oxidising substances promote corrosion of the metal, by combining with hydrogen on the surface of the tin to form water.

Methods and Apparatus.

Since corrosion by a weak solution of citric acid is mainly influenced by the presence of oxygen, it was thought that the rate of attack might be followed by measuring the absorption of oxygen. For this reason, the

apparatus used was a closed system designed so that any changes in the gaseous phase could be observed. The arrangement was such that the gases could be analysed at the end of an experiment; this permitted a comparison between the oxygen-equivalent of the metal in solution and the actual absorption of oxygen. The details of the apparatus are shown diagrammatically in Fig. 1 and were as follows:

The wide-mouthed bottle (A) of about 250 c.c. capacity, unless otherwise stated, was fitted with a double-bored rubber stopper and connected by capillary tubing, of about 1 mm. bore, to a gas-burette (B) of 50 c.c. capacity graduated in 0·1 c.c., which in turn communicated with a levelling tube containing mercury (C). A second capillary tube (D) fitted into the stopper was clipped up during a corrosion test. This facilitated such operations as the initial exhaustion of air from the bottle, or the transference of gas from the bottle into the burette at the end of an experiment.

The bottle was filled to a definite mark with the corroding medium and the metal test-piece suspended from a glass hook in the stopper. These test-pieces measured 3 inches × 1 inch and were about $\frac{1}{160}$th inch in thickness. They were drilled $\frac{1}{8}$ inch from the top with a small hole to fit the glass hook, and were hung so that 2 inches of the specimen was immersed in the corroding medium. A number of such units were set up, all alike as regards volume of corroding liquid, and size of headspace. The
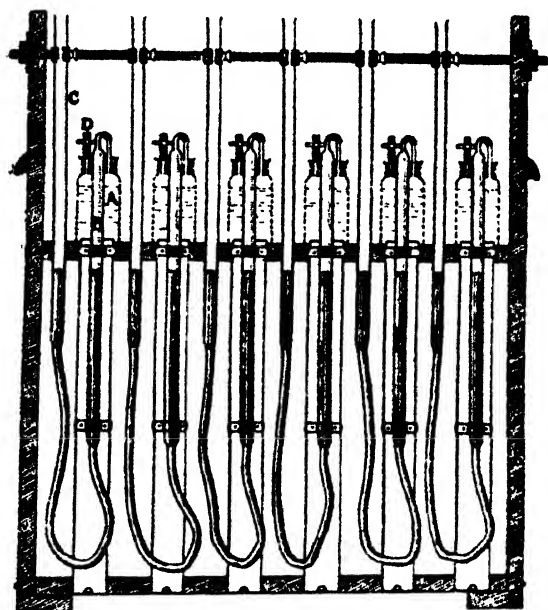
FIG. 1.—Diagram showing the Wooden Stand with Units attached.

bottles, as shown in the figure, were placed on a wooden stand of special construction and capable of holding ten units; the burettes and levelling tubes were supported by means of clamps fixed to a strong rail running along the top of the stand. These units when fitted up were carried into a thermostat room, and held at 25° C. during the period of the test. This temperature was maintained throughout all the corrosion tests subsequently described.

Purity of the Tin.—An analysis of the sheet tin used in these experiments was as follows:—

	per cent.
Tin	99·14
Copper	0·41
Antimony	0·25
Lead	0·13
Iron	0·035
Other impurities	0·035
	100·000

Preparation of the Test-strips.—These were treated with "O" Hubert emery paper to remove any oxide film, then heated in boiling absolute alcohol to remove grease, and finally dried and placed in a dessicator. The loss in weight, before and after the period of immersion, was taken as a measure of the corrosion.

The Corroding Media.—In most of the experiments the corroding solutions contained five grammes of citric acid per litre of water, and the hydrogen-ion concentration of the solution was varied by using sodium citrate as buffer. The actual amounts of sodium citrate added per litre of solution, and the corresponding p -values obtained by means of the quinhydrone electrode were :—

p_H 2·41 – 5 gm. citric acid; no sodium citrate per litre of solution.
,, 3·11 ,, ,, ,, + 1·5 gm. ,, ,, ,,
,, 4·03 ,, ,, ,, + 4·5 ,, ,, ,, ,,
,, 5·04 ,, ,, ,, + 15·0 ,, ,, ,, ,,
,, 5·54 ,, ,, ,, + 40·0 ,, ,, ,, ,,

Varying the hydrogen-ion concentration by use of a buffer seems preferable to the dilution method which involves great reduction in total acidity in the less acid solutions.

Elimination of Oxygen.— In the experiments conducted in the absence of air, the latter was removed from the corroding medium and headspace of the corrosion bottles by means of a Cenco " Hyvac " pump, and replaced
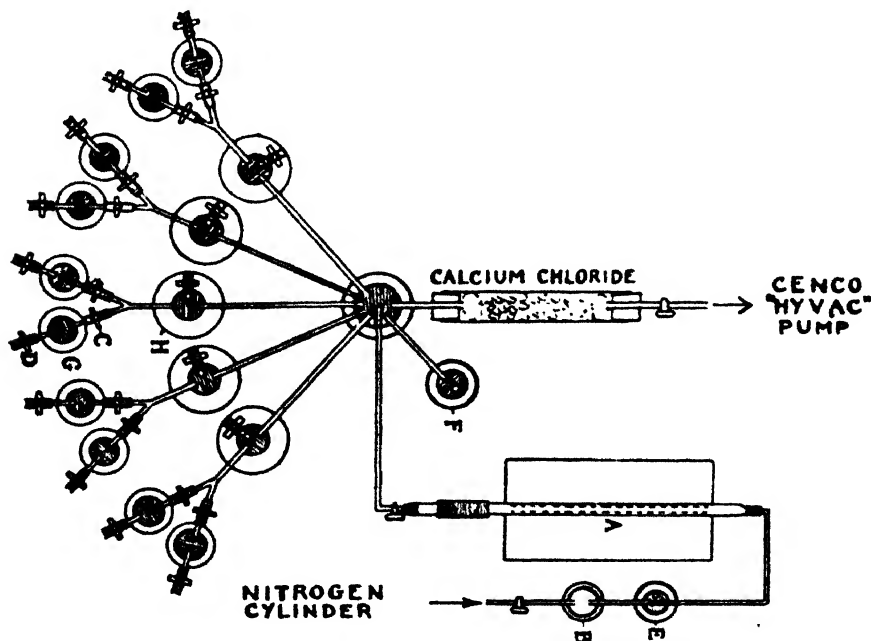
FIG. 2.—Plan (diagrammatic) of Apparatus for the Elimination of Air from Corrosion Vessels.

with oxygen-free nitrogen. The apparatus for this operation is shown diagrammatically in Fig. 2. The procedure was as follows :—

The whole apparatus was exhausted with the metal strips in position in the corrosion bottles, it was then filled slowly with nitrogen from a cylinder, which first passed through the electrically heated silica tube (A) containing red-hot copper gauze; in order to secure freedom from oxygen these

operations were repeated. The corrosion bottles (G), containing pure nitrogen were then isolated from the rest of the apparatus by means of screw-clips (C). The remainder of the apparatus was exhausted again, and the different corroding media, previously warmed to $25°$ C., were drawn into the five intermediate bottles (H) from a separating funnel inserted into a tube provided for that purpose. Each intermediate bottle contained enough liquid to fill the pair of corrosion bottles attached to it. The liquid was exhausted and allowed to boil for a short time under vacuum to remove dissolved oxygen. Glass tubes leading into a beaker of water were inserted into the outlet tubes of the corrosion bottles and liquid was forced into these bottles from the intermediate bottles, under pressure from the nitrogen cylinder, by opening first the inlet clips (C), and secondly the outlet clips (D). When the liquid reached the desired level in the corrosion bottles the inlet clips were closed. The outlet clips were then closed, and the bottles were ready to be attached to the gas-burettes.

The rate of passage of nitrogen into the apparatus was regulated with the help of the gas washing cylinder (B) containing sulphuric acid, and the bottle (E) containing mercury which also acted as a safety valve. The barometer tube (F) was useful in indicating the efficiency of the vacuum pump and the pressure of nitrogen in the apparatus. With this arrangement five pairs of uniformly treated units were obtained in which the elimination of oxygen was almost complete. (In later experiments an improved method was employed for the elimination of oxygen, see page 611.)

Experimental.

1. The Effect of Variation of Hydrogen-ion Concentration in the Absence of Air.—The bottles in which the strips were immersed were not attached to gas-burettes, as in this case no appreciable alteration in the volume of gas due to hydrogen was anticipated. After a period of immersion of twenty-eight days the gas in the headspace was collected and analysed; as was expected the hydrogen present only amounted to a doubtful trace. The test-pieces were removed from the liquids and washed, first in hot water, followed by cold water and alcohol, then dried on filter paper and finally placed in a desiccator. The loss in weight of duplicate specimens was very small and they showed practically no signs of corrosion (see Table I.). The figures indicate a slight decrease in corrosion from the most acid to the least acid end of the series.

TABLE I.

p_H of Solutions.	2·41.	3·11.	4·03.	5·04.	5·54.
Loss in weight in gm. . . .	0·0026	0·0019	0·0016	0·0012	0·0011
	0·0019	0·0016	0·0014	0·0012	0·0010
Average loss	0·0023	0·0018	0·0015	0·0012	0·0011

It must be pointed out, in connection with this experiment, that it is difficult to eliminate oxygen completely, especially over a prolonged period, when rubber is used in the apparatus. It is possible that traces of dissolved oxygen remained in the solution, even after the double exhausting with the vacuum pump. The solutions were not heated above $25°$ C. as the excessive boiling, induced by the vacuum pump at the higher temperature,

might have caused too great an alteration in the concentrations of the solutions. Furthermore, the use of heated copper gauze, for the removal of oxygen from the supply of nitrogen, was not so efficient as the method described below, which reduces the residual oxygen to less than 0·01-0·02 per cent. It was thought, therefore, that a proportion of the corrosion might be due to the presence of very small amounts of oxygen, and, to prove this point, an experiment was conducted in which further refinements for the exclusion of oxygen were adopted. This experiment differed from the previous one in the following respects :—

(1) The glass vessel used was specially designed to reduce the use of rubber to a minimum.

(2) The corroding solution, containing five grammes of citric acid per litre, was de-aerated by boiling and cooling *in vacuo*, in addition to evacuation with the " Hyvac " vacuum pump.

(3) Oxygen was removed from the nitrogen by the method of Kautsky and Thiele,[14] which consisted essentially in forcing the nitrogen from a cylinder through a porcelain filter-candle immersed in a strong alkaline solution of s o d i u m hydro-sulphite.

The loss in weight of the strip after a period of 28 days was only 0·0006 gm., being equivalent to less than 0·06 c.c. of oxygen assuming the tin to be in the stannous condition, an amount which almost certainly exceeds that which could be accounted for by any residual oxygen. From this result, it is evident that a great part of the corrosion reported in the previous experiment was due to the presence of a small amount of residual oxygen. Curve A of Fig. 3 is based on the result of this more critical experiment.

FIG. 3.—The Effect of Variation of Hydrogen-ion Concentration on the Corrosion of Tin in the Presence and Absence of Air.

2. **The Effect of Variation of Hydrogen-ion Concentration in the Presence of a Limited Supply of Air.**—A preliminary experiment was carried out in which specimens were immersed in the corroding liquids and allowed to corrode for a period of ten days with a limited supply of air in the headspace.

The results of this experiment in quadruplicate are illustrated by

Curve B of Fig. 3. Inspection of the strips after immersion showed that the attack was confined chiefly to the liquid-air interface in the less acid solutions; at p_H 2·4, however, this was not so evident, a well-marked corrosion zone occurring just below the surface. The daily burette readings showing the progressive decrease in total volume of gas did not represent the actual absorption of oxygen, as a small amount of carbon dioxide was evolved during the experiment. The absorption of oxygen was determined by analysis of the residual gases, and it was found that the volume of oxygen absorbed exceeded that which was necessary to convert tin to the stannic condition. It was thought that this discrepancy might be due to the formation of carbon dioxide through the activity of moulds which were observed in the solutions after the test.

A further experiment was conducted under sterile conditions, since it seemed desirable to verify this point. The details of the test were similar to those described previously, but differed in the following respects :—

(1) The period of the corrosion test was 28 days which ensured complete absorption of oxygen during the experiment.

(2) The corrosion bottles were of slightly larger capacity than those used previously, and were calibrated by means of glass beads, to give equal volumes of 280 c.c. The volume of the corroding solution was regulated so that the headspace was as nearly as possible 60 c.c. in each case. The units were clipped up during the experiment and were not attached to gas-burettes, as this simplified sterilisation.

(3) The solutions were sterilised by heating for half-an-hour in a steamer on two successive days, compensation being made for the liquid lost during this treatment. The corrosion bottles were sterilised by heating for 2 hours at 150° C. and the rubber stoppers, glass tubing and rubber-connections by heating in an autoclave for 30 minutes at 15 lbs. pressure. The test-pieces were heated in boiling absolute alcohol for half-an-hour. The apparatus was assembled under conditions which minimised the possibility of contamination by micro-organisms.

At the end of the experiment, the gases in the headspace were analysed (see Table II.).

TABLE II.

p_H of Solutions.	Volume f Gas in c.c. at N.T.P.				
	Total.	Carbon Dioxide.	Oxygen.	Nitrogen.	Hydrogen.
2·41	45·3	0·6	0·1	44·6	Nil.
3·11	44·0	0 7	0·1	43·2	,,
4·03	44·3	0·7	0·1	43·5	,,
5·04	44·4	0 8	0·1	43·5	,,
5·54	45·0	0·8	0·1	44·1	,,

From these figures, it is seen, that only a trace of oxygen remained at the end of the experiment and that some carbon dioxide was evolved even under sterile conditions, although not quite as much as in the former experiment. Since no moulds could be found in the solutions under these conditions, the presence of carbon dioxide may be taken to indicate oxidation of the citric acid. Slight variations in the headspaces of individual units were unavoidable, but, since the loss in weight of the strips

is nearly proportional to the absorption of oxygen, a correction may be made for these differences. Curve C, of Fig. 3, is based on this slight correction. The absorption of oxygen was determined by subtracting the residual oxygen from that which was present originally in the headspace, the latter being calculated from the nitrogen found by analysis at the end of the test. The volume of oxygen absorbed at different p_H-values is given in Table III.

TABLE III.

p_H of Solutions.	2·41.	3·11.	4·03.	5·04.	5·54.
Volume of oxygen originally present (in c.c. at *N.T.P.*) . . .	11·1	10·8	10·9	10·9	11·0
Volume of residual oxygen (in c.c. at *N.T.P.*)	0·1	0·1	0·1	0·1	0·1
Volume of oxygen absorbed (in c.c. at *N.T.P.*)	11·0	10·7	10·8	10·8	10·9

It is impossible to compare the absorption of oxygen with the oxygen-equivalent of the metal in solution, unless the state of oxidation of the metallic ions is known. For this reason two methods for estimating stannous tin in the presence of citric acid and sodium citrate were investigated.

(1) Titration of the stannous tin with $N/100$ iodine in an atmosphere of carbon dioxide, using starch as indicator.

(2) The addition of a standard solution of ferric chloride in excess, and back-titration with a standard solution of titanium chloride in an atmosphere of carbon dioxide, using ammonium thiocyanate as indicator.

The results of this investigation led to the following conclusions :

The first method was unsatisfactory when the concentration of sodium citrate exceeded 1 per cent., as in solutions of p_H 5·0 and 5·5, and the concentration of tin exceeded 0·002 per cent. With lower concentrations the errors were negligible. The second method proved to be satisfactory, but it was necessary to add before titration enough hydrochloric acid to make the solution twice normal with respect to this acid, otherwise oxidation of the stannous salt by ferric chloride was slow and caused inaccuracies in judging the end-point.

In estimating small amounts of stannous tin, as was the case in this experiment, direct titration with $N/100$ iodine appeared preferable to a method involving back-titration ; for this reason, the first method was adopted. The concentration of stannic tin was calculated by subtracting the weight of stannous tin, as estimated, from the total tin in solution, *i.e.*, the loss in weight of the strips. The results for the experiment in duplicate are shown in Table IV.

TABLE IV.

p_H of Solutions.	2·41.	3·11.	4·03.	5·04.	5·54.
Total tin from loss in weight (in gm.)	0·0504	0·0483	0·0459	0·0450	0·0450
Stannous tin by analysis (in gm.) .	0·0039	0·0026	0·0011	0·0010	0·0010
Stannic tin by difference (in gm.) .	0·0465	0·0457	0·0448	0·0440	0·0440

By calculating the volume of oxygen used in the formation of the above quantities of stannous and stannic tin, it is possible to compare the oxygen-equivalent of the total tin in solution with the volume of oxygen absorbed. This comparison is seen in Table V.

TABLE V.

p_H of Solutions.	2·41.	3·11.	4·03.	5·04.	5·54.
Oxygen absorption found by gas analysis (in c.c.)	11·0	10·7	10·8	10·8	10·9
Oxygen-equivalent of the stannous tin (in c.c.)	0·4	0·2	0·1	0·1	0·1
Oxygen-equivalent of the stannic tin (in c.c.)	8·7	8·6	8·4	8·3	8·3
Oxygen-equivalent of the stannous and stannic tin (in c.c.) . .	9·1	8·8	8·5	8·4	8·4
Oxygen excess (in c.c.) . . .	1·9	1·9	2·3	2·4	2·5

The discrepancy, therefore, between the volume of oxygen absorbed and the oxygen-equivalent of the tin in solution, shows an increase with decreasing acidity. Since the experiment was conducted under sterile conditions, this discrepancy must be due to oxidation of the citric acid and, possibly, the sodium citrate used as buffer, and is responsible for about two-thirds of the decrease in corrosion with decreasing hydrogen - ion concentration, which is seen in Curve C of Fig. 3. The remaining third is due to the more complete oxidation of the stannous tin to the stannic condition in the less acid members of the series.
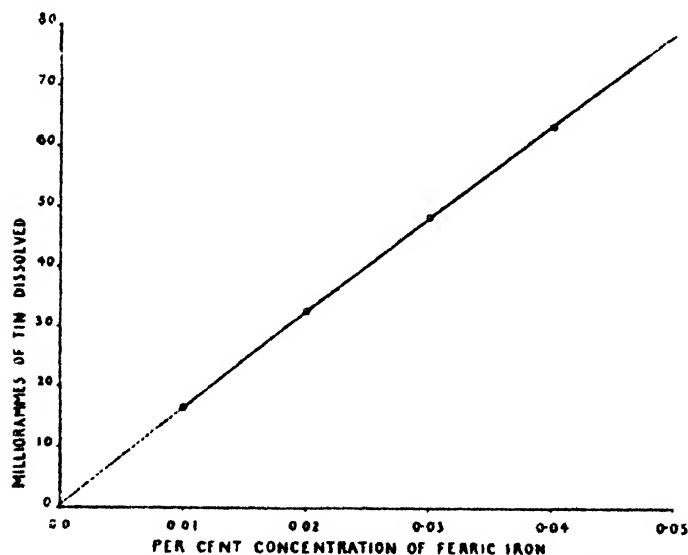
FIG. 4.—Corrosion of Tin by Ferric Citrate in a Solution containing 5 grammes of Citric Acid per Litre.

3. The Effect of an Oxidising Substance in Solution in the Absence of Air.—The oxidising substance chosen for these experiments was a solution of ferric citrate which was prepared by dissolving pure ferric hydroxide in citric acid. The corroding solutions consisted of a known amount of ferric iron, as ferric citrate, and five grammes of citric acid per litre. It was necessary to prepare these solutions

immediately before each experiment, as slight reduction of the ferric iron occurred on standing. The apparatus and corroding solutions were freed from oxygen and replaced by oxygen-free nitrogen, as described on page 611.

(1) *The Effect of an Increasing Concentration of Ferric Iron in Solutions Containing 0·5 per cent. of Citric Acid.*—The corrosion specimens were immersed in solutions (175 c.c. in each case) containing 0·01, 0·02, 0·03, 0·04, and 0·05 per cent. of ferric iron, respectively, as ferric citrate. The results showing the loss in weight of duplicate specimens, after a period of three days, is recorded by the curve of Fig. 4, which shows that an almost linear relationship exists between the concentration of ferric iron and the corrosion of tin. The fact that the extension of the graph (the dotted portion in the figure) does not pass through the zero point for the solution of tin, is in close agreement with the result obtained for corrosion of tin in the absence of air (see Curve A of Fig. 3).

(2) *The Effect of Ferric Iron in Solution at Varying Hydrogen-ion Concentration.*—The solutions contained the same proportions of citric acid and sodium citrate as in previous experiments (see p. 609). The concentration of ferric citrate was constant, 100 c.c. of solution, of which 215 c.c. was used in each test, containing 0·05 gm. of ferric iron. The p_H-values of the solutions were determined by the glass electrode, and it was found
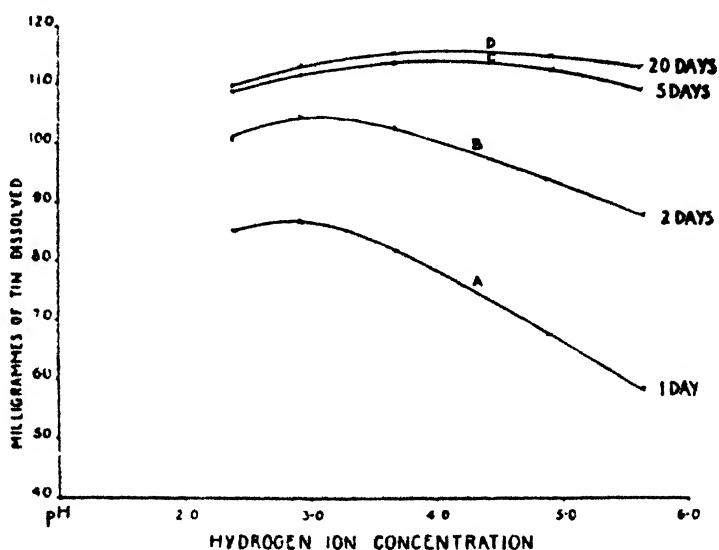
Fig. 5.—The Effect of Ferric Citrate on the Corrosion of Tin in Solutions of varying Hydrogen-ion Concentration.

that these were influenced considerably by the presence of ferric citrate.*

Experiments were carried out over periods of 1, 2, and 5 days, but, as none of these periods was long enough for the complete reduction of the ferric iron in the less acid units, a further test was conducted over a period sufficiently long to ensure the complete disappearance of the yellow colour; this required 20 days.

The results for the different periods are shown diagrammatically by Curves A, B, C, and D, respectively, of Fig. 5. Inspection of the strips after the test revealed no marked attack at the liquid-air interface, as is the case when oxygen was present, and corrosion was general over most of the immersed portion.

Examination of the curves shows that the greater part of the corrosion

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* The p_H-range became 2·38, 2·93, 3·68, 4·88, and 5·65.

occurred within a period of five days. It is apparent also, that the velocity of corrosion is retarded at first by a reduction in acidity, but, as the reaction proceeds, the attack becomes greatest quantitatively in the solutions of lower acidity. This effect is due to the fact that the final equilibrium, between tin in the stannous and stannic conditions, is affected by the hydrogen-ion concentration. Analysis of the solutions at the end of the twenty days' period proved that the ferric salt oxidised some of the tin to the stannic condition in the most acid members of the series, whereas it remained entirely in the stannous condition in the least acid members. Since the total amount of available oxygen used in the reactions necessary to bring tin into solution is constant, it follows that the differences in the total weight of tin dissolved are due, mainly, to the differing distribution of the available oxygen between stannous and stannic citrates formed at the various hydrogen-ion concentrations. There seems no doubt that the slight fall in corrosion which occurs at the less acid end of Curve D (Fig. 5) is due to a slight oxidation of the citric acid, or sodium citrate, by the ferric salt.

4. The Effect of Ferrous Citrate in Solutions of Varying Hydrogen-ion Concentration in the Presence of a Limited Supply of Air.—It was shown in the previous experiment, that an oxidising substance, such as ferric citrate, caused more rapid corrosion of tin than that which occurred in the presence of air (compare Figs. 3 and 5). Since a ferrous salt is readily oxidised to the ferric condition in the presence of air, it was thought that the presence of ferrous iron in solution would accelerate the corrosion of tin by acting as an oxygen-carrier through alternate oxidation and reduction, and that the attack might be influenced also by the hydrogen-ion concentration of the solution. An experiment was conducted, therefore, with corroding solutions buffered as before, but containing in addition 0.005 per cent. of ferrous iron.

FIG. 6.—Apparatus showing the Method of delivering Known Volumes of a Solution of Ferrous Citrate in an Atmosphere of Nitrogen.

Experimental.—A solution of ferrous citrate was prepared by dissolving pure iron wire in a de-aerated 1 per cent. solution of citric acid. The solution of ferrous citrate was displaced, by means of oxygen-free nitrogen, into a round-bottomed flask (A) (see Fig. 6), previously exhausted of air and refilled with nitrogen. Flask (A) was fitted with a glass tube (B) and a double delivery tube (C), which communicated with a graduated burette (D). With the glass stopper (E) in one position, solution could be displaced into the burette by opening

tap (F) ; in the reverse position, solution could be displaced from the burette into the bottle (H) by pressure of nitrogen and by opening tap (I), tap (F) being closed. The vessels (G) and (J), respectively, contained water which prevented access of air during these operations.

The iron in the solution, which was completely in the ferrous condition, was estimated by titrating in the usual manner with a standard solution of titanium chloride. The solutions containing the buffer were prepared separately from the solution of ferrous citrate, and were poured into the intermediate bottles (H) (see Fig. 2). These were de-aerated after being sterilised in steam, on two successive days, to minimise infection by micro-organisms. The solution of ferrous citrate was run directly from the burette into the bottles (H) by means of the side-tubes and rubber connections shown in the diagram ; in this way access of air was prevented during its addition. In preparing the buffer solutions corrections were made for—

(1) the slight concentration which occurred during sterilisation,
(2) dilution by the addition of the solution of ferrous citrate,
(3) the excess of citric acid contained in the solution of ferrous citrate, the final acidity being the same as in previous experiments.

These solutions containing 0·005 per cent. of ferrous iron were displaced into the corrosion bottles, in the usual manner, and were freed from nitrogen by exhausting before being connected with the gas-burettes, which contained 100 c.c. of air. Thorough mixing of the gases during the experiment was ensured by raising and lowering the levelling tubes several times at regular intervals. The burette readings are not recorded for reasons stated under Experiment 2. The results as shown by the loss in weight of the strips are given by Curve A of Fig. 7 ; Curve B, of the same figure, is reproduced from Curve B of Fig. 3 for comparison.

FIG. 7.—The Effect of Ferrous Citrate in Solution on the Corrosion of Tin by Air, at varying Hydrogen-ion Concentration.

Inspection of these curves clearly indicates the catalytic influence of ferrous iron in accelerating corrosion, its effect being particularly apparent at a hydrogen-ion concentration of about p_H 3·0, for reasons to be discussed later. After the experiment, the corroding solutions were colourless in the more acid range, but showed an increasing depth of colour, due to ferric iron, with decreasing acidity from p_H 4·0 to 5·5. The ferrous iron was estimated by the method of Hill[15] and the ferric iron calculated, by difference, from the total iron present in solution. The results are recorded in Table VI.

The stannous tin in solution was estimated by the titanium chloride method previously mentioned (see page 613). In this case, however, a

TABLE VI.

p_H of Solutions.	2·41.	3·11.	4·03.	5·04.	5·54·
Total iron (per cent.) . . .	0·005	0·005	0·005	0·005	0·005
Ferrous iron (per cent.) . . .	0·005	0·005	0·0046	0·0038	0·0036
Ferric iron (per cent.) . . .	0·0	0·0	0·0004	0·0012	0·0014

correction was necessary for the ferric iron present in the less acid solutions, since the addition of hydrochloric acid necessary for the titration, induced an immediate reduction of the ferric iron, an equivalent of stannous tin being oxidised to the stannic condition. The stannic tin in solution was calculated by subtracting the weight of stannous tin from the total tin as determined by the loss in weight of the strips. The results are illustrated diagrammatically by Curves C and D, of Fig. 7, the former curve representing the quantity of stannous tin and the latter the stannic tin.

Discussion.

In the preliminary remarks, it was pointed out that tin is protected from corrosion because of its high hydrogen-overvoltage. An experiment recorded in this paper proves that tin is practically unattacked by a weak solution of citric acid, when oxygen is excluded. Further experiments show that corrosion proceeds slowly in the presence of oxygen, and much more quickly when oxidising substances are present in solution. This form of corrosion, in which the hydrogen is depolarised, is quite distinct from the normal acid-type in which gaseous hydrogen is evolved. Wilson [16] stated that the rate of corrosion is proportional to the rate of diffusion of oxygen to the metal, in all cases, where depolarisation is the important factor. This being so, it is not surprising that, when oxygen is present, the corrosion of tin is confined mainly to the liquid-air interface. This attack of the metal is highly concentrated at the surface of the corroding solutions in the less acid members of the series, but at p_H 2·4 it is distributed over a wider area. It is possible that the sodium citrate used as a buffer is in some way responsible for this difference. In the presence of an oxidising substance in solution, such as ferric citrate, corrosion is general over most of the immersed portion, and no noticeable surface corrosion is evident when oxygen is excluded.

According to Chapman [6] tin is dissolved by a 5 per cent. solution of tartaric acid, in the presence of air, forming stannous tartrate; whereas, experiments by the author (see p. 615) prove that, with a 0·5 per cent. solution of citric acid in the presence of a limited supply of air, most of the metal in solution is present in the stannic form, and that oxidation was rendered more complete by a further lowering of the hydrogen-ion concentration. These apparently conflicting results are reconciled by the work of Foerster and Dolch,[17] which shows that although Sn—Sn^{++}, not Sn—Sn^{++++}, is the stable system both in acid and alkaline solution, yet, the presence of divalent tin in the alkaline solution is obscured by very rapid oxidation. It is certain, therefore, that a reduction in acidity favours oxidation of the stannous tin in solution to the stannic condition.

Curve B, of Fig. 3, represents the rate of corrosion of tin in the presence

of air, since a considerable proportion of the original oxygen remained in the headspaces at the end of the experiment. The velocity of corrosion showed a maximum at about p_H 3·0, and it is thought that the presence of traces of iron or other impurities in the tin (see p. 608 analysis of the tin) are responsible for the observed acceleration, as a similar but even more marked acceleration is brought about by the addition of a small amount of iron to the corroding solutions (see Curve A of Fig. 7).

Curve C, of Fig. 3, represents the total corrosion produced by a given volume of air, all the oxygen having been absorbed. The fall in corrosion, which is seen with decreasing hydrogen-ion concentration, is partly accounted for by the more complete oxidation of the stannous tin in solution to the tetravalent condition, and to a still greater extent to the oxidation of the citric acid (and possibly the sodium citrate) which definitely increases with decreasing acidity (see p. 614). A parallel case is afforded by the work of Walton and Graham,[18] which shows that a decrease in acidity increases the rate of oxidation of dicarboxylic acids by hydrogen peroxide, in the presence of certain catalysts. On the other hand, the possibility of an induced oxidation of the sodium citrate, used as a buffer, is suggested by the work of Dhar[19] in which it is reported that the oxidation of a solution of stannous chloride simultaneously induces oxidation of sodium formate and oxalate.

The effect of the presence of an oxidising substance in solution on the corrosion of tin, in the absence of free oxygen, is illustrated by the curves in Figs. 4 and 5. The curve in Fig. 4 shows an almost linear relationship between the concentration of ferric iron in solution and the corrosion of tin. This result is in agreement with the work of Van Name and Hill.[13]

The effect of solutions of varying hydrogen-ion concentration containing ferric citrate, over different periods, is illustrated by Curves A, B, C and D of Fig. 5. From these curves, it is apparent that corrosion occurs initially with greater rapidity in the more acid members of the series, but, as the reaction proceeds, the attack becomes increasingly greater in those of lower acidity. This effect is due to the fact that a decrease in acidity retards oxidation of the stannous tin in solution by the ferric salt, consequently, the efficiency of the available oxygen as a corroding agent increases correspondingly. That an increase in acidity promotes oxidation of a stannous compound by a ferric salt finds support in the work of Kahlenberg.[20] The slight fall in corrosion, from about p_H 4·0 to p_H 5·7 in Curve D, is evidently due to oxidation of the citrate-ion by the ferric salt, which lessens the quantity of the latter available for corrosion.

These results throw light on the mechanism of the corrosion of tin by a 0·5 per cent. solution of citric acid, containing ferrous citrate, in the presence of air. In comparing Curves A and B of Fig. 7, it is seen, that the effect of the ferrous salt is to increase the rate of corrosion of tin by air throughout the whole of the p_H-range studied; this is evidently due to the ferrous salt acting as an oxygen-carrier by alternate oxidation and reduction. The acceleration is particularly marked at a hydrogen-ion concentration of about p 3·0, and, it is significant, that this acidity corresponds with the maximum concentration of stannous tin in solution (see Curve C). It is obvious, that the oxygen used in converting tin from the stannous to the stannic condition is not available for corrosion, hence the fall in the curve at other acidities.

Summary.

1. Corrosion of tin is negligible in the absence of oxygen and within the range of hydrogen-ion concentration studied.

2. In the presence of oxygen, corrosion decreases with decreasing acidity from a hydrogen ion concentration of p_H 3·1 to p_H 5·5 ; the slight increase which is observed from p_H 2·4 to p_H 3·1 is possibly due to the traces of iron, or other metals, which were present as impurities in the tin. Decreasing the acidity increases the tendency for oxidation of stannous tin to the stannic condition, although most of the tin in solution is in the stannic form throughout the whole p_H-range. A discrepancy exists between the volume of oxygen absorbed, and that which is calculated from the oxygen-equivalent of the tin in solution. This discrepancy increases with decreasing hydrogen-ion concentration and is due to oxidation of the citric acid and, possibly, the sodium citrate used as a buffer.

3. The addition of a small amount of ferrous citrate to the corroding solutions causes a marked acceleration in the corrosion of tin by air, over the whole p_H-range, especially at about p_H 3, which is probably due to the catalytic action of the iron as an oxygen carrier.

4. Tin is readily attacked by a 0·5 per cent. solution of citric acid containing ferric citrate, in the absence of oxygen, and an almost linear relationship exists between the concentration of ferric iron and the metal dissolved. Decreasing the hydrogen-ion concentration retards the rate of attack initially, but the final corrosion is actually slightly greater at low than at high acidity. This is due to the fact that a decrease in acidity retards oxidation of the stannous tin in solution by the ferric salt ; consequently, the efficiency of the available oxygen, as a corroding agent, increases correspondingly.

BIBLIOGRAPHY.

[1] Food Investigation, Special Report, No. 40, 1931.
[2] H. Fleck, *Répert. Chim. Anal.*, 1, 424, 1858.
[3] M. Traube-Mengarini, and A. Scala, *Z. Koll.*, 10, 113, 1912.
[4] A. Wagner, *Dingler's Journ.*, 221, 259, 1876.
[5] W. P. Jorrissen, *Chem. News*, 111, 79, 1915.
[6] A. C. Chapman, *J. Chem. Soc.*, 103, 775, 1913.
[7] C. L. De Fouw, *Pharm. Weekblad.*, 55, 1497, 1918.
[8] K. B. Lehmann, *Arch. Hyg.*, 63, 67, 1907.
[9] F. P. Hall, *J. Amer. Chem. Soc.*, 4, 440, 1883.
[10] W. G. Whitman, and R. P. Russell, *J. Ind. Eng. Chem.*, 17, 348, 1925.
[11] O. P. Watts, and N. D. Whipple, *Trans. Am. Electrochem. Soc.*, 32, 257, 1917.
[12] H. J. Prins, *Proc. Acad., Amsterdam*, 23, 1449, 1922.
[13] R. G. Van Name, and D. U. Hill, *Am. Journ. Sci.*, 42, 301, 1916.
[14] H. Kautsky, and H. Thiele, *Z. anorg. Chem.*, 152, 342, 1926.
[15] R. Hill, *Proc. Roy. Soc.*, 107, 205, 1930.
[16] R. E. Wilson, *J. Ind. Eng. Chem.*, 15, 127, 1923.
[17] F. Foerster, and M. Dolch, *Z. Elektrochem.*, 16, 599, 1910.
[18] J. H. Walton, and D. P. Graham, *J. Amer. Chem. Soc.*, 50, 1641, 1928.
[19] N. R. Dhar, *Z. anorg. Chem.*, 144, 289, 1925.
[20] L. Kahlenberg, *J. Amer. Chem. Soc.*, 16, 314, 1894.

THE EXTENT OF DISSOCIATION OF SALTS IN WATER. PART III.

By W. H. Banks, E. C. Righellato, and C. W. Davies.

In Parts I. and II.[1] the dissociation constants of several salts in water were calculated from conductivity data. We have now examined the available figures for uni-univalent and uni-bivalent salts in the hope of supplementing the earlier results, but the search has been rather disappointing. Complete reliance cannot be placed on several of the series of measurements reported since they fail, on extrapolation, to give additive values for the mobilities of the ions. The results obtained are shown in Tables I.-III., the methods of calculation being those of the earlier papers.

Uni-univalent Salts.

Table I. gives the results for uni-univalent salts at 18°. m is the concentration in gm.-moles per litre, and a the calculated degree of dissociation ; K is the dissociation constant derived on the assumptions that the activity of the undissociated part of the salt is equal to its concentration, and that the mean activity coefficient of the ions is the same as in a potassium nitrate solution of the same ionic strength. The conductivity figures were taken from " International Critical Tables," Vol. VI.

TABLE I.

m	CsNO₃.		NaClO₃.		NaBrO₃.	
	a.	K.	a.	K.	a.	K.
0·05	0·966	0·95	0·989	3·0	0·991	3·6
0·1	0·947	0·99	0·986	4·0	0·983	3·3

These results fall into line with those already obtained. The dissociation constants of the nitrates of the alkali metals are found to be: Li, > 5 ; Na, 3·9 ; K, 1·37 ; Cs, 0·97. For the chlorates, bromates, and iodates, the results found are :

		ClO₃.	BrO₃.	IO₃.
Na	.	3·5 ?	3·5	3·0
K	.	1·5	2·2	2·0

The variations in each horizontal row are probably no greater than the experimental error.

Table II. gives some results at 25°. The conductivity data at 25° are not sufficiently accurate and numerous for systematic treatment, but the figures available for the alkali metal halides indicate that Onsager's equation can be extended to higher concentrations at 25° in the same way as at 18°. The conductivity figures on which Table II. is based are again taken from " Int. Crit. Tables," Vol. VI.

The dissociation constants previously found from the more reliable figures at 18° are included in the table for comparison. The agreement between

[1] *Trans. Faraday Soc.,* **23**, 354, 1927 ; **26**, 592, 1930.

TABLE II.

	m.	0·02.	0·05.	0·1.	0·2.
KNO_3 $K_{18°} = 1·37$	α K	— —	0·983 1·94	0·968 1·69	— —
$AgNO_3$ $K_{18°} = 1·20$	α K	— —	0·986 2·13	0·968 1·67	0·951 1·74
$KClO_3$ $K_{18°} = 1·49$	α K	0·985 1·05	0·969 1·04	0·955 1·18	— —

the new and the old values must be considered satisfactory, for with such highly dissociated salts small errors in the conductivity figures have a big effect upon K.

Uni-bivalent Salts.

Table III. gives some new figures for uni-bivalent salts. These have been calculated exactly as in the former paper.[2] m is the concentration in gm.-mols. per litre, and α the fraction of bivalent radical existing in the form of intermediate ion according to the scheme: $BU_2 \rightarrow BU + U$; $BU \rightleftharpoons B + U$. The third column shows the ionic strength, the fourth gives the "Ostwald" constant, $k' = \dfrac{m_B \cdot m_U}{m_{BU}}$, and the values of the disso-ciation constant given in the last column are calculated from the Debye-Hückel equation:

$$\log K = \log k' - 2\sqrt{\mu} + \Sigma B \mu.$$

The values of ΣB given in the table were obtained graphically; potassium chromate and oxalate were assumed to have the value $\Sigma B = 1·05$ previously found for potassium sulphate.

TABLE III.

	m.	α.	μ.	$\log k'$.	$\log K$.
$(NH_4)_2SO_4$ $\Sigma B = 0·56$	0·005	0·072	0·01428	− 0·906	− 1·137
	0·01	0·109	0·02782	− 0·811	− 1·131
	0·025	0·157	0·06715	− 0·607	− 1·087
	0·05	0·192	0·1308	− 0·420	− 1·070
	0·1	0·233	0·2534	− 0·235	− 1·100
$Ba(BrO_3)_2$ $\Sigma B = 1·04$	0·0025	0·028	0·00743	− 0·767	− 0·931
	0·005	0·040	0·01470	− 0·630	− 0·855
	0·01	0·065	0·02870	− 0·555	− 0·864
	0·02	0·095	0·05620	− 0·440	− 0·856
K_2CrO_4	0·05	0·094	0·1406	− 0·037	− 0·639
	0·1	0·095	0·2810	+ 0·259	− 0·507
$K_2C_2O_4$	0·025	0·018	0·0741	+ 0·422	− 0·245
	0·05	0·025	0·1475	+ 0·586	− 0·027
	0·1	0·045	0·2910	+ 0·618	− 0·154

[2] Part II., *Trans. Faraday Soc.*, **26**, 592, 1930. The conductivity and viscosity data are again taken from " Int. Crit. Tables," Vols. V. and VI.

It is of interest to find that ammonium sulphate is somewhat weaker than the corresponding potassium salt; this is the reverse of what has previously been reported for the nitrates.[3] Barium bromate is slightly stronger than the corresponding nitrate, and in this, as in the complete dissociation of its halides, barium resembles the alkali metals. Potassium chromate is slightly stronger than the corresponding sulphate. Finally, it is interesting to find that potassium oxalate is definitely more highly dissociated than either sulphate or chromate.

In addition to the salts mentioned, the chlorides and nitrates of bivalent manganese, cobalt, nickel, copper, and zinc have been examined. The mobilities of these ions are not accurately known, so a quantitative treatment of the data has not been attempted; but Table IV. shows the conductivities of the salts at 0·5 N (Heydweiller's data, taken from "Int. Crit. Tables," Vol. VI.) after application of the empirical viscosity correction previously adopted, i.e., the figures give values of $\Delta\eta^{\frac{1}{2}}$ where η is the relative viscosity of the solution. A small error in this correction will be unimportant, since the size of the correction is almost the same for all these salts.

TABLE IV.

	Zn.	Cu.	Ni.	Co.	Mn.	Ca.
Chloride	72·0	70·3	74·1	68·7	69·6	77·6
Nitrate	69·8	70·1	69·6	68·6	69·6	67·4

From a comparison of these figures several conclusions can be drawn : (1) calcium chloride is known to be completely dissociated; the mobility of the calcium ion is 51·3,[4] and that of the zinc ion is 45·5, a difference of 5·8 units at infinite dilution, or about two-thirds of this at the concentration considered. Since the conductivity of zinc chloride is 5·6 units lower than that of the calcium salt, dissociation must be nearly but not quite complete in zinc chloride at 0·5 N. (2) The mobility of the nitrate ion is 3·7 units lower, at infinite dilution, than that of the chloride ion. Zinc nitrate therefore appears to be a slightly stronger salt than the chloride, and possibly completely dissociated. (3) The mobility of the copper ion at infinite dilution is 0·4 units higher than that of the zinc ion, so that copper nitrate is as highly dissociated as the corresponding zinc salt. (4) From similar arguments copper chloride is not so highly dissociated as the nitrate, and appears to be definitely a "weaker" salt than zinc chloride. (5) Mobility values are lacking for nickel, cobalt, and manganese, but it is probable that the chlorides and nitrates of these metals are highly dissociated; in no case is there such a marked difference in conducting power of chloride and nitrate as is found with the calcium salts (and to a much greater extent with the corresponding barium salts). (6) If these figures are to be trusted, the nitrates of cobalt and manganese, like those of zinc and copper, are stronger salts than the chlorides, but the reverse is true of the nickel salts. An attempt to correlate the results so far obtained will be made in a later paper.

[3] MacInnes and Cowperthwaite, *Trans. Faraday Soc.*, **23**, 400, 1927.
[4] Mobility values from Davies, *Conductivity of Solutions*, p. 181, 1930.

Activity Coefficients of Uni-bivalent Salts.

If the stoichiometric activity coefficient of a salt is known, and also its degree of dissociation, the true mean activity coefficient of the ions can be calculated. This has been done for a bi-bivalent salt [1] and for uni-univalent salts,[5] and for the latter the true ion activity coefficients were found to show new regularities. To derive the necessary equation for a uni-bivalent electrolyte, consider the salt BU_2, which ionises as follows: $BU_2 \rightarrow BU + U$; $BU \rightleftharpoons B + U$. The stoichiometric activity coefficient, γ, is given by the equation $\gamma^3 = \dfrac{a_\pm^3}{4m^3}$, where m is the molal concentration of the salt, and $a_\pm$ is the measured mean activity of the ions. If the fraction of the radical B existing in the form of intermediate ion is a the actual concentration [6] of the divalent ion is $(1 - a)m$ and the concentration of the univalent ion is $(2 - a)m$; the true mean ion activity coefficient, $f_\pm$, should therefore be calculated from the equation

$$f_\pm^3 = \frac{a_\pm^3}{(1 - a)(2 - a)^2 m^3}, \text{ or } f_\pm = \frac{\gamma}{\sqrt{(1 - a)\left(1 - \dfrac{a}{2}\right)^2}}.$$

This equation has already been applied by Fromherz [7] to lead chloride. Table V. shows its application to all the available data; we have included results for lead chloride since our values for this salt are somewhat greater than those found spectrometrically by Fromherz and Lih.[8] Column 1 of Table V. gives the molal concentration of salt, column 2 the stoichiometric activity coefficient: column 3 gives the fraction of divalent ion associated, these values being taken from this or the previous paper,[1] column 4 gives the calculated ionic strength, column 5 its square root, and column 6 the ion activity coefficient. The figures are plotted in Fig. 1 against the square root of the ionic strength. The upper points are values of $(\log f_\pm + 1)$, and a continuous line has been drawn through the points for barium chloride. The lower series of broken lines show the stoichiometric activity coefficients plotted in the same way (right-hand scale of co-ordinates) against the square root of the " stoichiometric " ionic strength.

There are some minor discrepancies in the upper series of points. The values of $f_\pm$ for cadmium chloride are lower than those for other salts ; this difference might be real, or due to errors in the a values, but it is less than the possible errors in the activity data, which at these low concentrations are certainly less accurate than the other data tabulated. Also, the lead nitrate values are high, especially in the most dilute solutions ; this is almost certainly due to the method of extrapolation [9] used in determining γ, for the same anomaly is present in the uncorrected points as may be seen by comparing the lower curve for lead nitrate with those for other salts.

It is apparent that, with these doubtful exceptions, the same is true of these uni-bivalent salts as of the uni-univalent salts previously examined.[5] The corrections for incomplete dissociation entirely remove the anomalies in the activity figures, and lead to ion activity coefficients which are the same in dilute solutions for all salts of the same valence type. At higher

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[5] Blayden and Davies, *J. Chem. Soc.*, 949, 1930; Davies, *ibid.*, 2410, 1930.
[6] We have not converted the molar concentrations of our dissociation data into molalities. The difference between the two at the highest concentration, 0·1M, is within the probable error of the a values.
[7] *Z. physikal. Chem.*, A153, 376, 1931.　　　　　　[8] *Ibid.*, 321, 1931.
[9] Compare Randall and Scott, *loc. cit.*

TABLE V.

	$m.$	$\gamma.$	$\alpha.$	$\mu.$	$\sqrt{\mu.}$	$f_{\pm}.$
BaCl$_2$[10]	0·002	0·850	—	0·006	0·07746	0·850
	0·005	0·784	—	0·015	0·1225	0·784
	0·01	0·724	—	0·03	0·1732	0·724
	0·02	0·655	—	0·06	0·2449	0·655
	0·05	0·561	—	0·15	0·3873	0·561
	0·1	0·494	—	0·3	0·5477	0·494
CaCl$_2$[10]	(Same as for BaCl$_2$ up to $m = 0.01$)					
	0·02	0·658	—	0·06	0·2449	0·658
	0·05	0·570	—	0·15	0·3873	0·570
	0·10	0·515	—	0·3	0·5477	0 515
PbCl$_2$[10]	0·002	0·803	0·086	0·005656	0·07521	0·852
	0·005	0·704	0·166	0 01334	0·1155	0 792
	0·01	0·612	0·263	0·02474	0·1573	0·745
	0·02	0·497	0·386	0·04456	0·2111	0·675
CdCl$_2$[10]	0·002	0·684	0·205	0·005180	0·07197	0·794
	0·005	0·569	0·345	0·01155	0·1074	0·744
	0·01	0·475	0·462	0·02076	0·1441	0·696
Pb(NO$_3$)$_2$[11]	0·005	0·773	0·084	0·01416	0·1189	0·819
	0·01	0·694	0·135	0·02730	0·1652	0·764
	0·02	0·600	0·205	0·05180	0·2276	0·696
	0·05	0·465	0·333	0·1167	0·3416	0·601
	0·1	0·369	0·443	0·2114	0·4597	0·530
Ba(NO$_3$)$_2$[12]	0·005	0·764	0·048	0·01452	0·1205	0·789
	0·01	0·695	0·077	0·02846	0·1687	0·733
	0·02	0·615	0·122	0·05512	0·2348	0·670
	0·05	0·497	0·221	0·1279	0·3577	0 584
	0·1	0·405	0·324	0·2352	0·4851	0·519
Na$_2$SO$_4$[12]	0·005	0·783	0·043	0·01457	0·1207	0·806
	0·01	0·719	0·053	0·02894	0·1702	0·719
	0·02	0·045	0·072	0·05712	0·2390	0·645
	0·05	0·537	0·117	0·1383	0·3720	0·583
	0·1	0·449	0·156	0·2688	0·5185	0·502

concentrations specific deviations of the normal type become of course too great to be ignored.

The great deviations of the activity data for uni-bivalent salts from the requirements of the Debye-Huckel equation have been recognised for some time. The explanation that has received the greatest volume of support in the recent literature is founded on the failure of the simplified equations of Debye and Huckel to account fully for the electrostatic interaction between oppositely charged spheres of small effective radius. Corrections based on various treatments have been suggested by Bjerrum,[13] Müller[14] and Gronwall, La Mer and Sandved,[15] and these can be made to account for the experimental results by choosing appropriate values for the mean effective

[10] Values of γ taken from a compilation of the data by Scatchard and Tefft, *J. Amer. Chem. Soc.*, **52**, 2281, 1930.
[11] Randall and Vanselow, *J. Amer. Chem. Soc.*, **46**, 2418, 1924.
[12] Randall and Scott, *ibid.*, **49**, 647, 1927.
[13] *Kgl. Danske Videnskab. Selskib, Math-fys. Medd.*, **7**, 9, 1926.
[14] *Physik. Z.*, **28**, 324, 1927; **29**, 78, 1928.
[15] *Physik. Z.*, **29**, 358, 1928.

diameter of the ions in each case.[16]   It seems to us impossible to reconcile this view with our figures, for instance, for the salts of the metals of Group II. ;   association is absent in 0·5 N solutions of barium chloride but is very considerable in barium nitrate, while cadmium chloride is a very weak salt
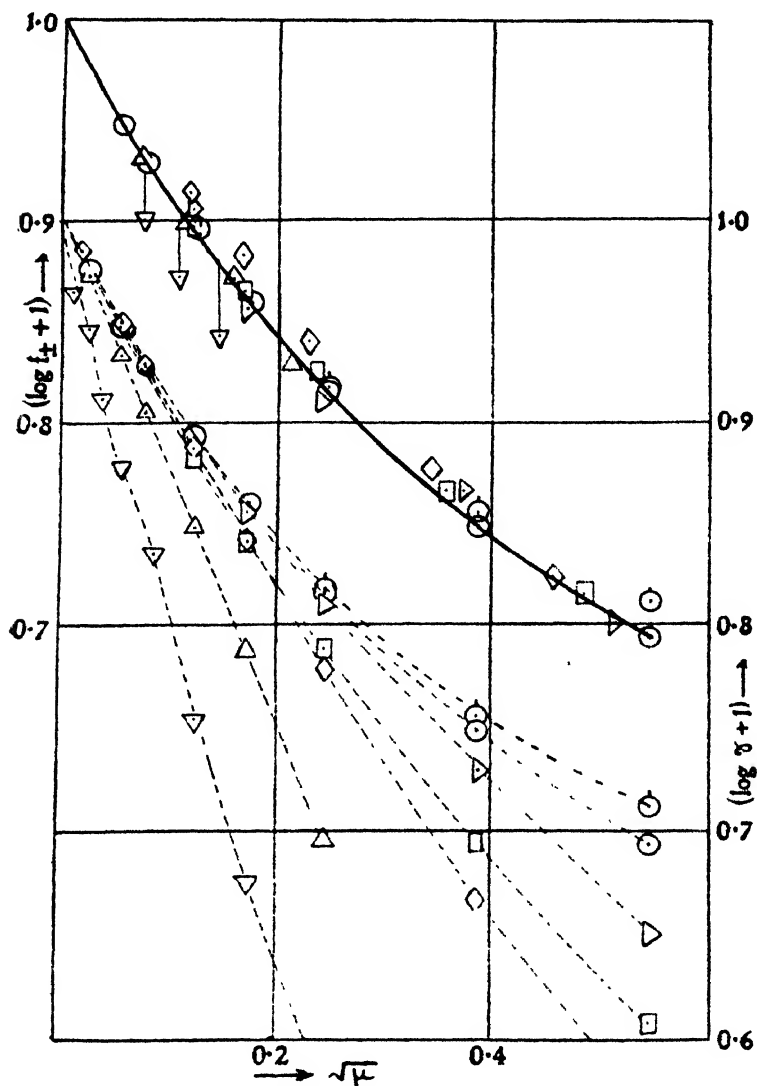
Log f + 1 (upper points), and log γ + 1 (lower points), for uni-bivalent salts.
⊙ CaCl$_2$; ⊙ BaCl$_2$; ▷ Na$_2$SO$_4$; ☐ Ba(NO$_3$)$_2$; ◇ Pb(NO$_3$)$_2$; △ PbCl$_2$; ▽ CdCl$_2$.

Fig. 1.

and cadmium nitrate shows only slight association.   Similar comparisons could be based on almost all the figures we have obtained.   In further developments of this theory, therefore, the " mean effective diameter " would

[16] See La Mer, *Trans. Amer. Electrochem. Soc.*, 1927; Bjerrum, *Ber.*, **62**, 1091, 1929 ; Scatchard and Tefft, *loc. cit.*

become a property of the salt rather than of the ions, that is, a "chemical" rather than a "physical" attribute.

There remain two alternatives. The deviations may be wholly due to chemical association, or they may be ascribed partly to this and partly to the limitations of the Debye-Huckel equation just referred to.[17] This second alternative is a reasonable one, but it does not appear to be favoured by the facts at present in our possession. What is found is a number of salts (*e.g.*, barium nitrate, sodium sulphate) exhibiting all possible degrees of "strength" from cadmium chloride upwards (*cf.* the broken lines in Fig. 1), and a second large group of salts (including all the halides as well as other salts of sodium and barium) which show in dilute solution no deviations from a uniform behaviour. Where a salt does show deviations it would seem necessary to ascribe them to the characteristics of the cation and the anion in their relationship with one another (and solvent), that is, to a "chemical" interaction. The second effect would seem to be negligibly small for most uni-univalent and uni-bivalent salts.

In conclusion it might be well to point out that the calculations of this and of previous papers have an immediate practical value which is unaffected by the theoretical question just discussed. It has been shown that the properties of dilute solutions of uni-univalent and uni-bivalent electrolytes—conductivities, transference numbers, freezing-points, solubilities, electrode potentials—can be correlated and quantitatively expressed by means of values for the dissociation constants of the possible products of ionic association. Any of the properties enumerated can be adapted to the calculation of these dissociation constants.

[17] See Scatchard and Tefft, *loc. cit.*

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REVIEW OF BOOK.

Chemische Bindung als electrostatische Erscheinung. Deutsche, von den Verfassern autorisierte Ausgabe von Li Klemm und Wilhelm Klemm. By A. E. VAN ARKEL und J. H. DE BOER. Med. 8vo. Pp. xx + 320. (Leipzig: S. Hirzel, 1931.) 15 gold marks.

This is an exceedingly valuable book. The title is perhaps a little misleading in that it suggests a restricted field of enquiry : one would like to be greatly daring, and call it "The New Chemistry," for it is nothing less. Chemists deal with molecules, and here they will find all about them, independent of the particular state of matter in which they happen to occur. With this broad generalisation before the reader, he is carried rapidly along from first principles of molecular physics through crystallochemistry, theory of solutions, change of state (quite properly, somewhat in the background), hydration, adsorption and surface energy. Classical electrostatics consume perhaps a trifle too much space, but the Heitler-London homopolar linkage comes in at the right place, and points the way to future conquests. Naturally, the authors do not claim anything very new for all this ; the merit of the book lies in the fact that there is nothing like it— in any language—with respect to the particular phenomena with which it deals, and between which it sets out to show the connection.

An example will make this clear. Ionic deformability is discussed in detail : it is emphasised how this quantity is derivable from the Stark Effect, series spectra, or refractivity, while applications follow for gases, solutions and crystals. It is difficult to see how the subject could be more widely treated, or with less respect for arbitrary partitions which frequently divide, with a maximum of inconvenience, physical laboratories from chemical ones.

Amongst much that is so good, one hesitates before offering a suggestion. Nevertheless, the reviewer proposes to query whether the evidence upon linkage which visible and infra-red spectra (for all states of matter) can provide has not been overlooked. Surely the results of the latter have not been fruitless, both as criteria between alternative molecular models, and as a subtle discriminant between different degrees of chemical binding. Again, the influence of the dielectric constant of a solvent is most important in determining the geometry of ionic groups in solution compared with their configuration in the crystal lattice. These matters conform to the spirit of the book exactly ; they are fundamentally electrostatic, and to reconcile the part which they have played with their omission from these pages is not easy.

To spend a little time upon the author-index is illuminating ; one travels long stretches between British names. It is only too true that the problem of chemical linkage—in the light of modern concepts—has received but short shrift in these islands. Perhaps this silent reproach will not go unheeded.

Finally, this is a volume which need not be kept in the research laboratory ; some of it is delightfully simple, and suitable for honours classes. It might well bear the sub-title " Molecular Physics without tears ".

F. I. G. RAWLINS.

DEPTH AND RIGIDITY OF SEDIMENT IN FLOCCULATED CLAY SUSPENSIONS.

By R. K. Schofield, M.A., Ph.D., and G. W. Scott Blair, M.A.

(*Soil Physics Department, Rothamsted Experimental Station, Harpenden, England.*)

If a suspension containing about 1 per cent. of flocculated clay is shaken up and then allowed to settle, the settling process can be divided into three clearly distinguishable parts.

(1) At first, settling is extremely slow. The suspension behaves like a very weak jelly. Very small rigid forces hold up the clay particles, so that for an appreciable time there is no perceptible disintegration. The length of time of this "induction" period is very arbitrary. The same sample does not show the same period in repeated sedimentations.

(2) After this, it appears that fissures are formed containing clear liquid. This rises through the suspension breaking up the jelly-like structure in its course. Very soon, the structure is completely broken up into floccules, and these then begin to settle down at a constant speed. The top of the sediment is flat and structureless, and, if scratched with a wire, the mark of the scratch is not retained. The settling curve over this part of the process is practically linear and the rate of settling is reproducible within narrow limits.

(3) As already described,[1] at a well-defined point, bumps and holes appear on the surface of the sediment. Any scratch made on the surface is retained, and the rate of settling becomes very much slower. The dynamics of the process have already been discussed in the letter quoted : in general we may compare this stage to the syneretic contraction of a gel. There is a definitely rigid structure of hydrated particles, from which water is slowly exuded. The contraction of the sediment does not appear to be caused by gravitational forces   However long we allow the sedimentation to proceed there is always a slow contraction going on, but it is possible to compare the heights of sediment to which a series of clays will settle if a suitable arbitrary time is chosen for the comparison. Provided that the time chosen is not too short, a comparison of different clays will lead us to conclusions independent of the time chosen. (If the time chosen is short, the variable induction period will render a comparison meaningless.)

The following questions at once arise :

(1) What is it that defines this height of sediment for a clay ? Is it perhaps defined by the strength of its rigid structure ?

(2) If samples of the same clay, which have been flocculated with (*a*) different ions, and (*b*) different quantities of the same ion, are compared, how will the volumes of sediment differ ?

[1] Schofield and Keen, *Nature*, **123**, 492, 1929.

(3) If a single sample of flocculated clay is shaken and then allowed to settle, and this process is repeated a number of times, will there be any progressive change in the volume of sediment or in the strength of the rigid structure ?

It was with a view to answering these questions that the work to be described in this paper was undertaken.

Apparatus.

In order roughly to measure the strength of the rigid forces in the settling suspensions, an apparatus was set up as shown in Fig. 1.

The suspension under investigation is poured into the beaker which stands on the suspended stage (A), and allowed to settle. When it is required to take a reading, the height of the sediment (h) is read off on the scale stuck to the beaker, and the glass ball (B),* which is suspended on a thread, is let down into the suspension. By means of an indicator fastened at the other end of the thread in such a way as to move over another scale (C), it is possible to lower the ball to such a height that its centre is placed 1 cm. below the surface of the sedimentary layer.

The stage on which the beaker stands is then drawn sideways by means of the thread attached to the wheel (D), the amount of sideways displacement (l) being measured on the scale (E). The thread on which the ball is suspended thereupon makes an angle with the vertical. During the first few seconds after the displacement this angle lessens, and if the suspension shows little or no rigid properties, becomes zero. In rigid suspensions, however, a certain displacement is retained, and it is found in general that the angle (θ) which is read off on the protractor (F) after about one minute decreases only quite slowly after this time. A reference point (G) is provided to eliminate parallax in reading the angle. Since the suspensions show but imperfect elastic properties there is a slow fall in θ if the stress is kept on indefinitely, but it is not difficult to determine the initial value with fair accuracy.

It is found that the value of θ is independent of l provided that l is sufficiently great. If l is too great the ball comes near the side of the beaker, and this creates undesirable complications. When the sediment is very compact, it is sometimes difficult to get the ball into its correct position without its being upset by the proximity of the bottom of the beaker. Should this happen a widely erratic point results. (An instance of this appears in the hydrogen clay curve (Fig. 2).)

Preparation of the Materials.

In order to be able to specify precisely the conditions under which the sedimentation of a clay suspension is taking place, it is necessary to know not only what salts have been added to an initially salt-free suspension, but also the cations in combination with the original clay. This is most readily done by first washing the clay with very dilute acid, thereby replacing exchangeable metallic cations by hydrogen ions. A clay so treated, and subsequently washed free from excess acid is spoken of as a "hydrogen clay," and a clay containing any specific metallic ion can readily be obtained from it by adding the corresponding hydroxide.

* Most conveniently of diameter about 5-7 mm.

Experimental Procedure.

A standard suspension of 5 per cent. Hydrogen clay was diluted down to 1 per cent. with a dilute solution of a base. The concentration of base required just to bring the suspension to a state of neutrality was determined previously by electrometric titration. Even so, it was found that Barium, Calcium, and Hydrogen clays were so sensitive to minute quantities of electrolytic impurities as to be flocculated under these conditions. From the conductivity of the supernatant liquor the concentration of electrolyte was calculated, assuming this to be chloride. The suspensions were shaken
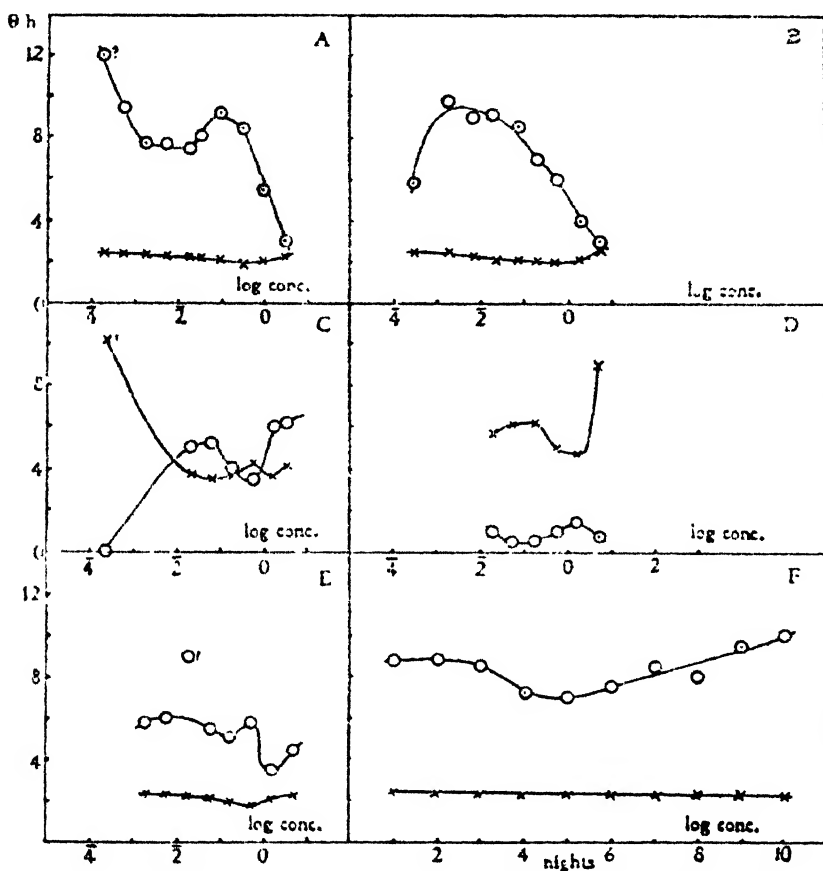
Fig. 2.—Sedimentation and rigidity for homoionic clays. (⊙ θ. × h.)

A. Ba⋅⋅ clay + BaCl₂.
B. Ca⋅⋅ clay + CaCl₂.
C. K⋅ clay + KCl.

D. Na clay + NaCl.
E. H clay + NaCl.
F. Ba clay + N/1000 BaCl₂ shaken up and left to settle over each night.

up and allowed to settle overnight, readings being taken after 16 hours settling. Each day, an appropriate amount of chloride was added as flocculant, and if there was any appreciable evaporation the suspensions were made up to their original volumes with distilled water, shaken in the evening, and a reading again taken the following morning. The Ca⋅⋅, Ba⋅⋅, K⋅, and Na⋅-clays were flocculated with the respective chlorides, the Hydrogen clay being flocculated with sodium chloride. As a control, a sample of the Barium clay just flocculated with BaCl₂(N/1000) was shaken and settled each day without the addition of further electrolyte.

The results are shown graphically in Fig. 2, in which the values of h and θ are plotted against the logarithmic normalities of the flocculants.

Conclusions.

It is clear from Fig 2 that our original questions may now be answered as follows :—

(1) There is no simple relationship between the final height of sediment and the strength of rigid structure as measured 1 cm. below the surface.

(2) Within wide limits there is no appreciable effect on the final height of sediment h, on the substitution of the hydrogen by Barium or Calcium, nor does the concentration of the corresponding chloride affect h except at very high concentrations.

(3) Persistent shaking and settling of a suspension of clay causes a slight regular fall in h, and there are also slight fluctuations in the strength of the rigid structure.

We may also conclude that :—

(4) The shape of the θ-concentration curves is very complicated, and cannot be fully explained at present.

(5) The Na$^{\cdot}$-ion, and to a less extent the K$^{\cdot}$-ion, cause the formation of a thixotropic gel having a big volume and comparatively low strength. The same process appears to be starting at very high concentrations in the case of the H$^{\cdot}$, Ba$^{\cdot\cdot}$, and Ca$^{\cdot\cdot}$ clays.

Accuracy in determining θ is not very great, and in any case the property seems to be subject to certain rather odd fluctuations, but the measurements are quite accurate enough to demonstrate without question the points set out above. Perhaps the most remarkable and unexpected of these is the constancy of the sediment volume under the conditions set out in (2). It therefore appears that under these conditions, the sediment volume depends only on the concentration and nature of the clay. What factors must be included under the heading "nature of the clay" has still to be ascertained, though degree of sub-division is certainly one. The fineness of subdivision is a soil property of considerable agricultural importance. The fundametal nature of sediment volume as revealed by this investigation suggests that it may prove of value in soil investigation.

Summary.

1. When a suspension of Hydrogen clay which has been flocculated by the addition of a small quantity of an electrolyte is left overnight the volume of the sediment after an arbitrary time (16 hours) is reproducible within narrow limits.

2. When shaken and left for a second period of 16 hours the sediment volume is usually about 2 per cent. less, and further repetitions cause similar progressive reductions.

3. Substitution of Ca$^{\cdot\cdot}$ or Ba$^{\cdot\cdot}$ for some of the exchangeable H$^{\cdot}$ does not change the sediment volume.

4. Addition of CaCl$_2$ and BaCl$_2$ respectively to these suspensions of substituted clays does not appreciably change the sediment volume up to a normality of chloride of about $N = 1$.

5. When the clay contains exchangeable Na$^{\cdot}$ or K$^{\cdot}$, high concentrations of the corresponding chlorides are required to flocculate the clay. In these cases and whenever the clay is suspended in a chloride of about normal strength or over, a thixotropic gel of larger volume is formed.

6. The strength of the rigid structure of the sediment depends on the exchangeable ions present and on the nature and concentration of the added salt. The relationships involved appear to be complex.

7. The reproducibility of the sediment volume obtained in dilute salt solutions suggests that a measurement of this quantity may be of use in soil studies.
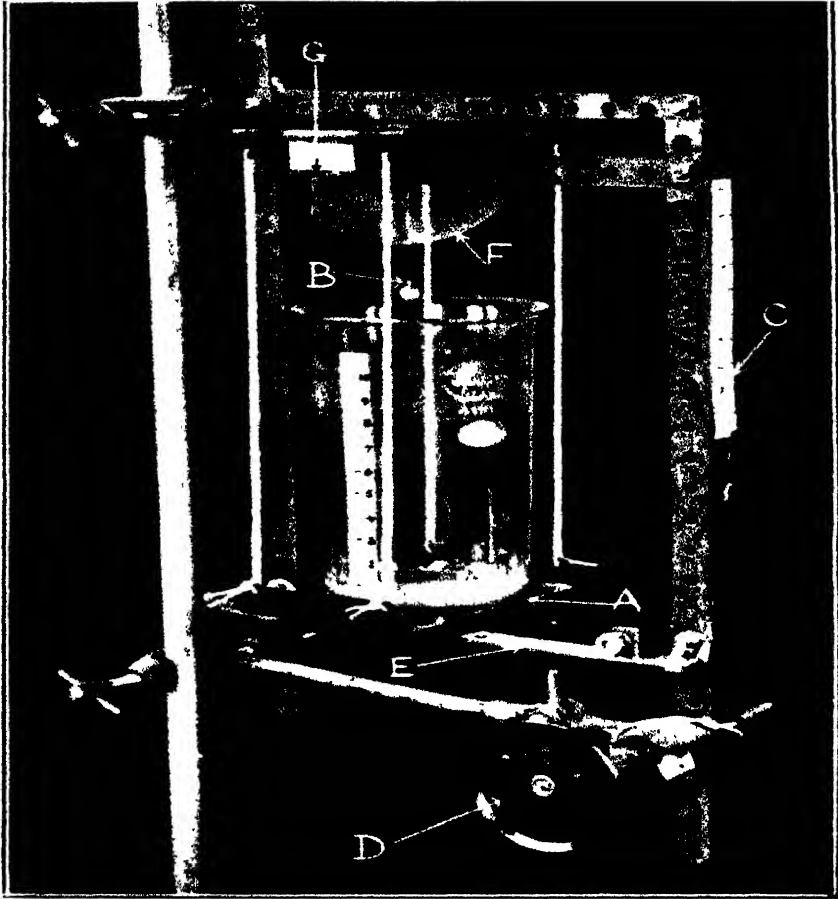
FIG. 1.
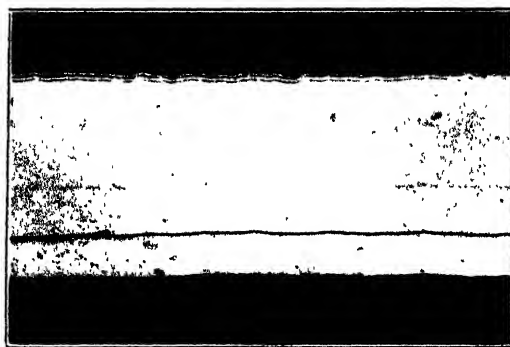
[A] Acidity of solution: f_H, 6·9, [7·1]. Brinell hardness no., 418.
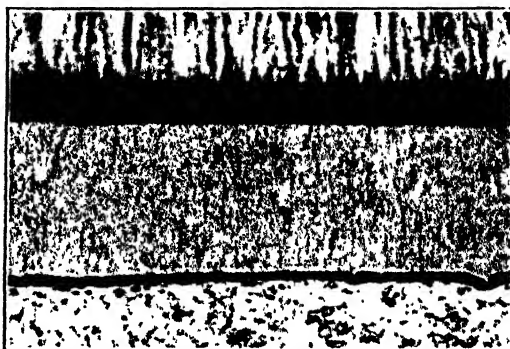
[B] Acidity of solution: f_H, 5·95, [6·15]. Brinell hardness no., 302.

[C] Acidity of solution: f_H, 3·75, [3·95]. Brinell hardness no., 187.

FIG. 3.—Solution Y. Microstructure of nickel deposits, showing the effect of change in acidity.

THE INFLUENCE OF ACIDITY OF THE ELECTROLYTE ON THE STRUCTURE AND HARDNESS OF ELECTRODEPOSITED NICKEL.

By D. J. Macnaughtan and R. A. F. Hammond.

During recent years, as a result of a number of investigations, increased knowledge has been acquired concerning the internal structure and physical properties of electrodeposited metals produced under certain definite conditions. This has proved to be of considerable value in securing electrodeposits suitable for certain specific purposes. The data obtained have not, however, proved adequate to enable a comprehensive generalisation, connecting the conditions of deposition with the structure and properties of electrodeposits, to be established. It has therefore been the object of this investigation to obtain further quantitative data connecting the effect of certain factors which operate during deposition with the properties of electrodeposited metals. Attention has been confined to nickel and deposition of this metal has been carried out under carefully controlled conditions in a number of typical solutions in which the acidity has been varied over a wide range. The deposits obtained have been examined and tested.

Previous Work on the Properties of Nickel Deposits.

In previous investigations [1, 2] in which one of the authors has been concerned, the Brinell hardness of nickel deposits produced in various solutions in a restricted range of acidity, *viz.* : p_H 5·3-5·5 (5·8-6·0 colorimetric) * have been determined.

A striking difference in the Brinell hardness numbers of the deposits from nickel sulphate solution was found to occur when it was buffered with ammonium sulphate and boric acid respectively. Hard deposits were produced in the solution containing ammonium sulphate, and soft deposits in the solution containing boric acid. The hard deposits were found to have a finer crystalline structure and a higher tensile strength and resistance to abrasion than the soft deposits ; while in the form of thin coatings such as are used in decorative plating the hard deposits, owing to greater smoothness, were found to be easier to polish.[2]

In a further investigation [3] in which the effects of other buffering agents, namely, sodium fluoride and sodium sulphate, were examined, it was again found that in the restricted p_H range 5·3 to 5·7 (5·8-6·0 colorimetric) investigated, deposits of the highest hardness and finest structure were obtained when the buffer salt was ammonium sulphate.

It has not proved possible to account for the results obtained in these investigations in terms of various hypotheses which have been put forward to explain the manner in which the conditions of deposition determine the crystal structure of the deposit.

Thus it has been suggested that during deposition there is a direct relationship between the cathode potential and the size of the crystals of the

* See page 635 for explanation why two values are given for p_H throughout.

633

deposit.[4] This view was not supported by the results of cathode potential measurements made during the production of coarse-grained and fine-grained nickel deposits respectively.[3]

The hypothesis that in the case of nickel (and of the other metals of the iron group), differences in crystal size of the deposit are primarily related to the amount of hydrogen discharged during deposition [5] could not be reconciled with the results of cathode efficiency determinations which showed that the amount of hydrogen discharged at the cathode was approximately the same in the case of various deposits of greatly differing structure and physical properties.[3]

It was therefore suggested by the authors that, in the case of nickel, co-deposited oxides might prove to be of importance in determining the size of the crystals of the deposit.[6]

This possibility has subsequently received support from the work of O'Sullivan, who found that as the p_H of the nickel depositing solution is raised there is a tendency for the deposits to become smoother and finally more brittle, and that this could be most satisfactorily explained as being due to the inclusion of an increasing amount of nickel hydroxide or a basic salt derived from the liquid adjacent to the cathode.[7]

In the present investigation, the method of judging the structure of the deposit by examination of its external appearance as used by O'Sullivan is replaced by quantitative determinations of the Brinell hardness together with micro-examination of the structure after etching.

Preparation of Salts of High Purity.

In view of the pronounced effect upon the properties of nickel deposits which may be caused by quite small amounts of impurity derived from the salts or from the anodes used, it was essential to prepare these materials in a state of high purity.

(*a*) **Nickel sulphate** of good quality (copper ·005 per cent., zinc ·004 per cent., iron ·002 per cent.) was first subjected to the permanganate treatment previously described,[8] whereby any organic matter present was removed, together with the traces of iron.

The nickel sulphate was subsequently carefully recrystallised and a highly pure product obtained.

(*b*) **Ammonium sulphate** of A.R. quality was dissolved in water and subjected to an oxidising treatment with potassium permanganate to remove traces of organic matter in a manner similar to that used in the purification of the nickel sulphate.

(*c*) **Potassium chloride and sodium fluoride** of A.R. purity were separately ignited in a platinum dish to a dull red heat to oxidise organic matter.

(*d*) **Boric acid** of A.R. quality was used.

Preparation of Nickel Anodes of High Purity.

Nickel anodes of high purity were prepared in a manner similar to that described previously.[3]

Composition of Solutions Used.

The composition of the solutions prepared from the salts of high purity are shown in Table I.

TABLE I.—COMPOSITION OF SOLUTIONS.

Solution Reference No.	Grammes Per Litre.					
	Nickel Sulphate, $NiSO_4$ $7H_2O$.	Ammonium Sulphate $(NH_4)_2SO_4$.	Boric Acid, H_3BO_3.	Potassium Chloride, KCl.	Sodium Chloride, NaCl.	Sodium Fluoride, NaF.
N	240	—	30	19	—	—
Y	120	21	—	8	—	—
F	240	—	30	—	7·85	5·8

As prepared the solutions had a p_H below 5. In order to bring each solution to the highest p_H at which the series of experiments could be commenced, they were treated in the following manner. The nickel sulphate was dissolved in distilled water and the solution boiled with a small quantity of nickel hydroxide. After filtration the other constituents which had been previously dissolved in distilled water were added. This procedure was adopted in order to avoid the precipitation of a basic borate which occurs in the case of the N and F solutions if the other constituents of the bath are present with the nickel sulphate when this is boiled with nickel hydroxide.

The nickel hydroxide suspension was prepared by adding a boiling solution of pure caustic potash to a boiling solution of purified nickel sulphate, the latter being in slight excess. The hydroxide precipitate was washed by decantation with distilled water until free from alkaline salts and afterwards filtered through sintered glass. The cake of hydroxide was then transferred to a bottle and shaken to give a suspension with distilled water.

Correction of p_H.

Throughout the investigation p_H measurements were made by the colorimetric comparator method using buffer standards. This method gives results which are considerably higher than the true values owing to the salt error.[9] In order to make the necessary corrections the p_H of a large number of samples of the three solutions used were tested over a wide range of acidity by both the quinhydrone electrode method and by the comparator method. In each solution the salt error was found to be fairly constant over the particular range of p_H which proved to be important in this investigation. The following corrections which are in substantial agreement with those published by Blum and Bekkedahl[9] based upon the results of the quinhydrone test, were applied to the results obtained by the colorimetric method :—

N solution   .   .   . — 0·5
Y   „   .   .   . — 0·2
F   „   .   .   . — 0·45

Buffer Characteristics of Solution.

Determinations were made of the buffer characteristics of the three solutions in the range of p_H used in the preparation of the deposits by suitably titrating 2 litre samples with $2N$ H_2SO_4. The p_H was ascertained after each acid addition by the colorimetric method. The results are shown graphically in Fig. 1, the p_H values plotted being values corrected as

above.   The curves commence at the p_H values of the solutions freshly prepared in the manner described.

The alternative method of determining the buffer characteristics by titrating an acidified solution with alkali has the advantage that a buffering curve may be obtained extending to the point at which precipitation of
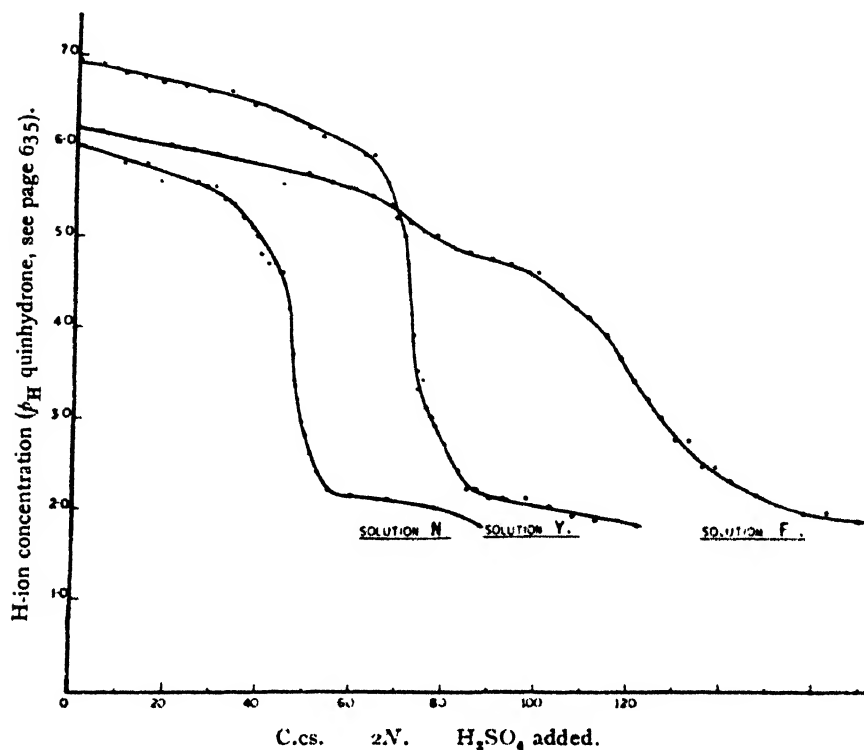
C.cs.   2N. H_2SO_4 added.
FIG. 1.

nickel hydroxide or a basic salt commences but is subject to experimental difficulties on account of the very slow rate of re-solution of the nickel hydroxide which is precipitated locally at the point at which alkali enters the solution during the later stages of the titration.

Both methods were used in the case of the Y solution and the buffering curves obtained showed close agreement.

Details of Deposition Experiments.

For deposition, round glass jars six inches in diameter were used, each containing 3 litres of purified solution. The jars were immersed in an electrically heated water bath, the temperature of which was thermostatically controlled within $\pm \frac{1}{4}°$ C. The cathodes consisted of $\frac{5}{8}$-inch hexagonal mild steel bars each $1\frac{1}{2}$ inches long which had been previously coated with a thin deposit of copper 0·001 inches in thickness. Each cathode was suspended by means of a soldered nickel wire so as to hang in the centre of a jar while four anodes, each approximately $4\frac{1}{2}$ ins. × 2 ins. in dimensions, were arranged at equal distances around the periphery of the jar. The anodes were hung in the solution from hooks of nickel wire.

In order to determine the cathode efficiencies, a copper coulometer was connected in series with the nickel baths. The size of the cathode in the

coulometer was chosen so as to maintain copper deposition at a current density of 10 amperes per sq. ft. (1·1 amps. per sq. dcm.).

The coppered steel cathodes after being weighed were subjected to cathodic treatment for a few seconds in alkali and then to a momentary dip in 10 per cent. sulphuric acid. This procedure cleaned the surface and had no perceptible effect upon the weight of the cathode. Each cathode was then swilled in distilled water and introduced into the nickel bath. Nickel deposition was carried out for a sufficient length of time to provide an adequate thickness of deposit for hardness testing (approximately 0·01 inch). On removal, after rinsing in water and alcohol, the specimens were dried and weighed.

During the deposition of nickel the p_H of the solution was carefully controlled.

When the production of two deposits at a particular p_H had been completed, sufficient sulphuric acid was added to lower the p_H of the bath by about one p_H unit. The new p_H was then kept constant whilst two further deposits were made.

Each deposit obtained was given a light polish with fine emery and its Brinell hardness determined, using a 1 mm. ball under a 10 kilogramme load. Six impressions were made on each specimen and each impression was measured across two diameters at right angles.

For micro-examination the specimens were thickly coated with a layer of electrodeposited copper and were cut through transversely near the centre, the sections thus obtained being ground and polished. The polished sections were etched with a mixture of nitric and acetic acids.

Determinations were made of the cathode potential over the range of p_H investigated in the Y solution, at the current density used for the production of the deposits.

The results are given in Table II.

TABLE II.—THE EFFECT OF CHANGE IN p_H ON THE CATHODE POTENTIAL.

Conditions of Deposition · Cathode Current Density 1·2 amps. per sq. dm. (11 amps. per sq. ft.). Temperature 35° ± ·5. Solution Y.

p_H of Solution.		Cathode Potential (Volts.)	Hardness of Deposit (Brinell Numbers.)
Quinhydrone Electrode.	Colorimetric.		
6·6	6·8	0·603	360
6·3	6·5	0·593	328
6·1	6·3	0·595	308
5·8	6·0	0·618	278
5·6	5·8	0·589	258
5·2	5·4	0·602	222
4·9	5·1	0·597	199
4·6	4·8	0·606	187
4·1	4·3	0·615	186
3·7	3·9	0·614	187
3·0	3·2	0·619	189
2·0	2·2	0·580	192

The results of deposition experiments are shown in Table III.

The results show that as the p_H is raised from the lowest to the highest value in the range investigated there is an increase in the Brinell hardness number of the deposits from 192 to 418 in the Y solution, from 178 to 285

TABLE III.—HARDNESS OF NICKEL DEPOSITED FROM SOLUTIONS CONTAINING :
(1) AMMONIUM SULPHATE (Y), (2) BORIC ACID (N), (3) BORIC ACID + SODIUM
FLUORIDE (F).

Depositing conditions : Temperature $35° \pm 0.5°$ C.   Cathode current density 1.2 amps.
per sq. dcm. (11 amps. per sq. foot).   Anode current density 0.13 amp./sq. dcm.
1.2 amps. per sq. ft.   Thickness of deposits about 0.01 inch.
     Highly purified nickel anodes and solutions prepared from specially purified
materials were used.

Reference. Number	Bath.	p_H Measurement.		Cathode Efficiency Per Cent.	Brinell Hardness No. 1 mm. Ball 10 kg. Load.
		Colorimetric.	Quinhydrone.		
Y 15	Y	7·10	6·90	—	418
Y 3	,,	6·75	6·55	99·3	368
Y 2	,,	6·75	6·55	—	341
Y 4	,,	6·15	5·95	99·5	302
Y 16	,,	3·2	3·0	—	217
Y 13	,,	2·0	1·80	67·1	194
Y 8	,,	4·90	4·70	98·8	194
Y 12	,,	3·05	2·85	94·8	192
Y 14	,,	2·0	1·80	64·9	191
Y 11	,,	3·05	2·85	95·2	188
Y 9	,,	3·95	3·75	98·6	187
Y 10	,,	3·90	3·70	98·6	186
Y 7	,,	4·95	4·75	—	184
Y 1	,,	6·75	6·55	99·1	—
Y 6	,,	5·0	4·8	98·3	—
N 15	N	6·2+	5·8	99·4	287
N 16	,,	6·2+	5·8	99·5	282
N 1	,,	6·1	5·6	99·1	226
N 2	,,	6·2	5·7	—	225
N 3	,,	6·2	5·7	99·3	203
N 13	,,	2·0	1·85	69·6	181
N 14	,,	1·90	1·75	80·0	174
N 12	,,	3·05	2·55	95·8	169
N 10	,,	4·0	3·5	99·0	166
N 4	,,	5·8	5·3	99·6	165
N 9	,,	4·0	3·5	99·0	163
N 8	,,	4·90	4·4	99·3	163
N 7	,,	4·85	4·35	99·2	157
N 5	,,	5·8	5·3	99·4	155
N 6	,,	5·0	4·5	98·7	—
F 12	F	6·6	6·15	99·3	379
F 15	,,	6·4	5·95	99·5	277
F 14	,,	6·4	5·95	99·5	260
F 3	,,	5·0	4·55	98·2	182
F 1	,,	6·0	5·55	99·4	178
F 2	,,	6·0	5·55	99·3	173
F 4	,,	5·0	4·55	98·3	165
F 11	,,	6·0	5·55	99·1	159
F 5	,,	4·0	3·55	96·8	157
F 6	,,	4·0	3·55	96·9	156
F 10	,,	2·0	1·8	79·8	153
F 13	,,	4·9	4·45	97·8	153
F 9	,,	2·0	1·8	77·3	151
F 8	,,	3·1	2·65	94·2	148
F 7	,,	3·1	2·65	94·4	141

in the N solution, and from 152 to 379 in the F solution.   The hardness,
however, does not increase uniformly with increase in p_H.   Thus in the N
and Y baths there is first of all a slight drop in hardness as the p_H is in-

creased over a considerable range and then a rapid rise in hardness occurs as a result of a relatively small further increase in p_H. In the fluoride bath there is an intermediate stage in which there is only a slight rise in hardness with increase in p_H; otherwise the general relationship of p_H and hardness in this bath is similar to that obtained in the N and Y baths. The results are shown graphically in Fig. 2.

The results of the micro-examination were as follows: (1) a deposit which had a Brinell hardness number in the range from 140-190 had a structure consisting of relatively large elongated crystals disposed with their
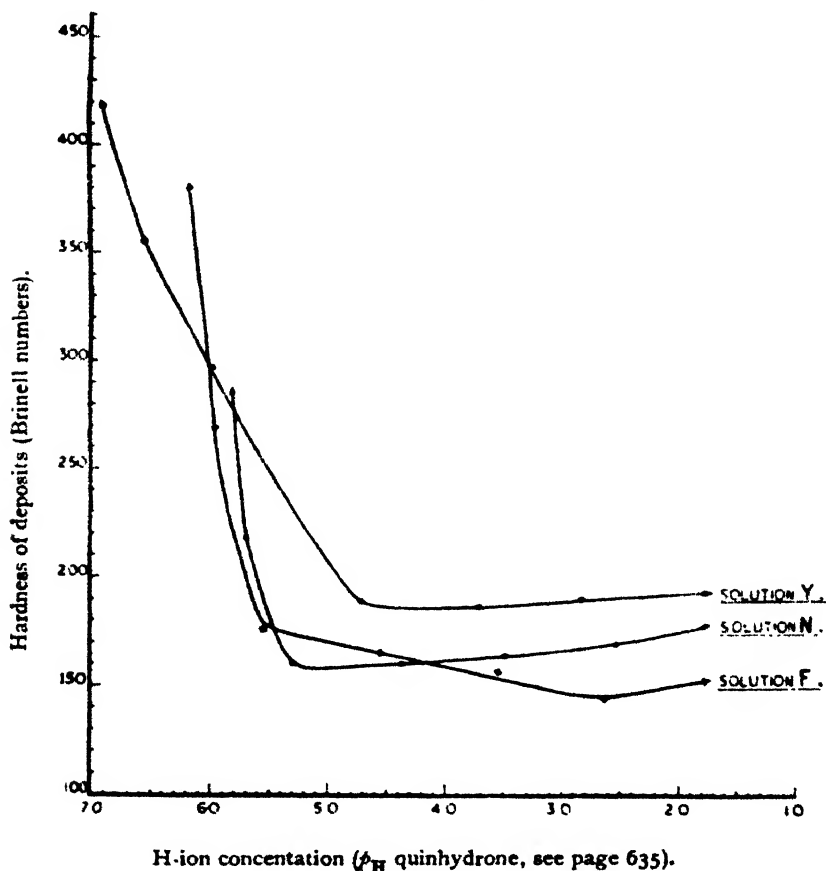
H-ion concentation (p_H quinhydrone, see page 635).
FIG. 2.

major axes in a direction normal to the cathode surface.   Typical examples of these deposits are shown in Figs. 3, 4, and 5 (C)*; (2) a deposit which had a Brinell hardness number in the range 190-260 showed a similar structure composed of smaller crystals—see Figs. 3, 4, and 5 (B); (3) a deposit which had a Brinell hardness number in the range 260-420 had an exceedingly fine structure which in the deposits of higher hardness was so fine as to be beyond the limits of resolution in the microscope—see Figs. 3, 4, and 5 (A).   Of the deposits produced in the p_H range 5·3 to 5·5 (5·8-6·0) which is generally used in the industrial deposition of nickel, those

* Fig. 3 faces page 633;   Fig. 4, page 640;   Fig. 5, page 641.

from the Y solution were hard and of fine structure, while those from the N and F solutions were soft and of relatively coarse structure. This confirms the results which have previously been published.[1, 2, 3] It is evident, however, that it is practicable to obtain hard or soft nickel deposits from any one of the three solutions by suitably adjusting the p_H.

(a) **Hard Deposits.**—The deposits of maximum hardness from the three solutions were produced by deposition at the highest p_H at which the solutions could be satisfactorily operated, this being just below the p_H at which precipitation of nickel hydroxide or a basic salt of nickel takes place in the bulk of the solution. As approximately as could be determined visually the precipitation occurs in the three solutions as follows :—

$$
\begin{array}{llllll}
N & . & . & . & . & p_H \ 6{\cdot}1 \ (6{\cdot}6) \\
F & . & . & . & . & \text{,,} \ 6{\cdot}1 \ (6{\cdot}6) \\
Y & . & . & . & . & \text{,,} \ 7{\cdot}4 \ (7{\cdot}6) \\
\end{array}
$$

The hardness of the deposits which were obtained somewhat below the precipitation p_H was as follows :—

	Hardness.	p_H.
N . . .	285	5·8 (6·2)
F . . .	379	6·15 (6·6)
Y . . .	418	6·9 (7·1)

A comparison of the microstructure of the hard deposits obtained from the three solutions shows the presence of cracks in the deposits obtained from the N and F solutions but not in those obtained from the Y solution —see Figs. 3, 4, and 5 (A). It is significant in this connection that the rate of change of hardness with p_H (in the range of p_H which results in the production of hard deposits) is much greater in the N and F solutions than in the Y solution. This is well shown in Fig. 2 by the difference in the slopes of the p_H-hardness curves. It is evident that relatively slight fluctuations in the p_H of the N and F solutions will produce much more pronounced changes in the hardness and structure of the deposits than in the case of the Y solution. Thus a change in p_H from 5·9 to 6·1 (6·35 to 6·55) in the F solution results in an increase in Brinell hardness of the deposits from 250 to 350, whereas a much greater change of p_H, from 5·5 to 6·5 (5·7 to 6·7) is necessary to effect a similar change in the hardness of the deposits from the Y solution. It seems likely that the effects produced by slight fluctuations in p_H, such as may easily occur during the production of thick deposits, may account for the cracking of the deposits owing to sudden changes of stress associated with changes in structure. This is being further investigated. The sensitiveness of the N and F solutions to change in p_H is not likely to be compensated for by their superior buffering properties, since the difference in the degree to which the three solutions are buffered in the high p_H range is not very great (see Fig. 1). As regards cathode efficiency, in the high p_H range (see Fig. 6) the results obtained were as follows :—

p_H Range.	Hardness Range.	Average Cathode Efficiency.
Y solution 5·5-6·9 (5·7-7·1) . . .	250 418	99·2 per cent.
N solution 5·75-5·8 (6·25-6·3) . . .	250-285	99·3 ,, ,,
F solution 5·9-6·1 (6·35-6·55) . . .	250-350	99·4 ,, ,,
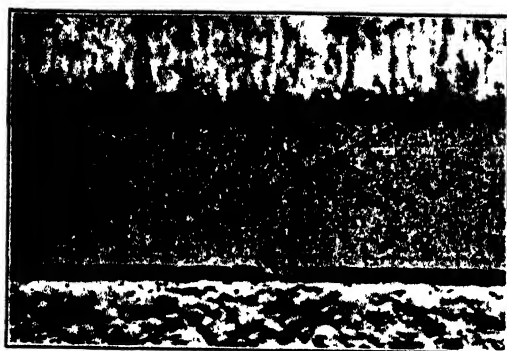
[A]. Acidity of solution: f_H, 5·8, [6·3]. Brinell hardness no., 287.
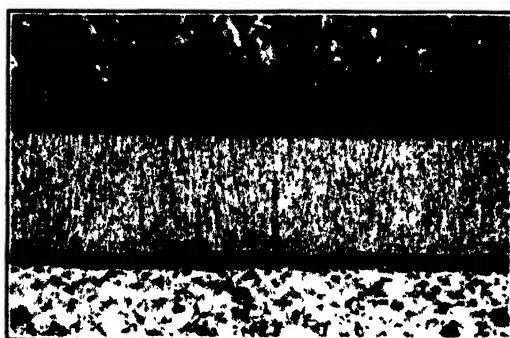
[B]. Acidity of solution: f_H, 5·7, [6·2]. Brinell hardness no., 203.

[C]. Acidity of solution: f_H, 5·3, [5·8]. Brinell hardness no., 165.

FIG. 4.—Solution N. Microstructure of nickel deposits, showing the effect of change in acidity.

[*See page* 639.

[A]. Acidity of solution: p_H, 6·15, [6·6]. Brinell hardness no., 379.
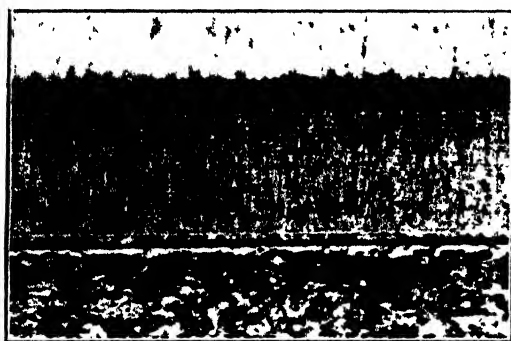
[B]. Acidity of solution: p_H, 5·95, [6·4]. Brinell hardness no., 260.
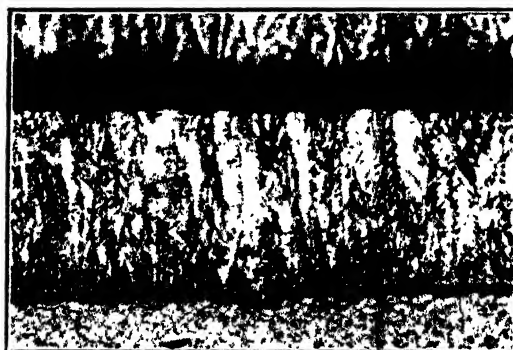
[C]. Acidity of solution: p_H, 2·65, [3·1]. Brinell hardness no., 141.

FIG. 5.—Solution F.   Microstructure of nickel deposits, showing the effect of change in acidity.

These results show that the cathode efficiency obtained in the range of p_H required for hard deposits is not greatly different in the three solutions.

It would thus appear that for the production of hard deposits the Y solution is superior to the N and F solutions both as regards obtaining maximum hardness and maximum soundness, *i.e.* freedom from cracks in the deposits. This confirms the conclusion previously reached by one of the authors that for the production of hard nickel deposits the solution should be buffered with an ammonium salt such as ammonium sulphate.

(*b*) **Soft Deposits.**—Soft deposits can be produced in all the solutions preferably at a p_H which is somewhat lower than the critical p_H at which a rapid rise in hardness commences. The critical p_H values are shown in Fig. 2 to be. N bath 5·3 (5·8), F bath 5·55 (6·0), Y bath 4·7 (4·9). As the acidity of the solution is increased below the critical p_H, there is a slight increase in the hardness of the deposits from the N and Y baths and a decrease or small increase, according to the degree to which the p_H is lowered, in the F bath; there is also a marked reduction in the cathode efficiency. In view of this latter effect it would therefore be generally advantageous to produce soft deposits at a p_H only slightly lower than the critical p_H. Under these conditions the cathode efficiency and Brinell hardness is as follows:—
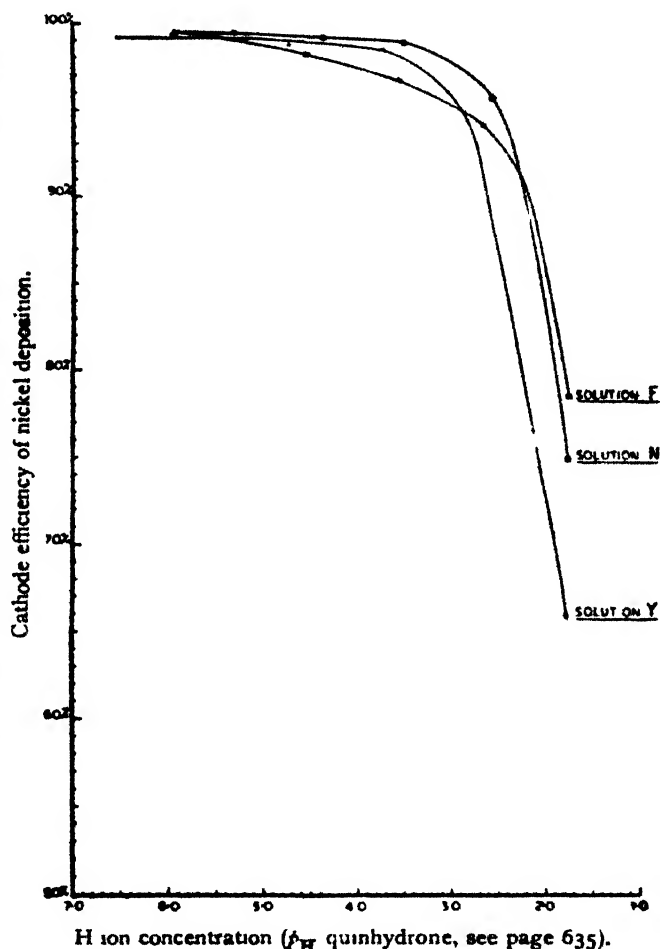
H ion concentration (p_H quinhydrone, see page 635).

Fig. 6.

p_H.	Cathode Efficiency.	Brinell Hardness No.
Y 4·5 (4·7) . . .	99·0 per cent.	186
N 5·0 (5·5) . . .	99·4 ,, ,,	158
F 5·3 (5·75) . . .	99·0 ,, ,,	174

These results show that when the p_H is adjusted so as to be slightly below the critical p_H soft deposits are obtained in all the solutions at approximately the same cathode efficiency.

A comparison of the buffering curves in Fig. 1 indicates that the N and F solutions are the most suitable solutions for the production of soft deposits at a moderately low p_H, e.g. p_H 4·5 (5·0).

Discussion of Results.

The fact that in each of the solutions investigated the effect of change of p_H on the properties of the deposit is similar, would appear to be of general significance. This appears to be confirmed by a consideration of the effect upon the structure of the deposit of the following : (1) current density, (2) cathode potential, (3) cathode efficiency.

(1) Current Density.

In the deposition of copper, and in certain cases in the deposition of other metals, it has been observed that at a low current density, a soft deposit of large grain size is produced, and that at a high current density a harder deposit of finer grain size is produced. Presuming that these conditions apply generally it has been suggested [10, 11] that this effect could be explained by the assumption that the electrical field of force at the cathode is an important factor in determining the position of the metal atoms at the moment of deposition. Thus the greater the intensity of the electric field relative to the atomic field of force at the cathode face the larger the proportion of atoms that will tend to be discharged in positions which do not coincide with positions on the lattice of the previously formed crystals. In this way there would be a tendency as the current density is increased and the intensity of the electric field is increased, for interference in the growth of crystals to occur, so that a more or less progressive refinement in grain size would take place.

The results obtained in the course of this investigation, however, show that in the case of nickel deposition the change from a soft deposit of large grain size to a hard deposit of exceedingly fine grain size may occur without any perceptible increase in current density. Thus in the range p_H 4·7 to 6·9 (4·9-7·1), in the Y solution the Brinell hardness numbers of the deposits increase from 190 to 418 and the structure changes from one which is coarsely crystalline to one which is exceedingly fine grained, yet the current density used was 1·2 amperes per sq. dm. (11 amps. per sq. ft.) throughout. Allowing for the rise in efficiency from 98·8 per cent. to 99·2 per cent. the increase in the effective current density from the point of view of nickel deposition is only 0·4 per cent. The insignificance of the current density under the conditions investigated in determining the structure is further shown in the range p_H 4·7 to 1·8 (4·9 to 2·0) when there is an actual rise in hardness although the effective current density of nickel deposition drops about 33 per cent. Similarly in the other solutions, N and F, under the conditions investigated no relationship between the variations in current density which arise as a result of changes in cathode efficiency and the properties of the deposit can be established.

(2) Cathode Potential and the Properties of the Deposit.

An assumption involved in the view discussed above is that the intensity of the electrical force at the cathode face varies in direct proportion to the current density. This is only the case, however, while the metal ion concentration on the cathode face remains constant. Usually, with rise in

current density the metal ion concentration tends to decrease. A more accurate index of the intensity of the electrical force at the cathode would appear to be the potential between the cathode and the adjacent liquid as this will be determined by both current density and metal ion concentration. Upon the reasonable assumption that a single metal atom has a higher solution pressure than a crystal, *i.e.*, an oriented group of atoms, Blum and Rawden [4] have suggested that a higher potential will be required to start a crystal nucleus at the cathode surface than to continue the growth of an existing crystal. They have, therefore, put forward the hypothesis that all factors that tend to increase the difference of potential between the cathode and the solution must favour the formation of nuclei, *i.e.*, new crystals, and in consequence the higher the cathode potential the finer grained and harder will be the deposit. [4]

The results obtained in the course of this investigation—shown in page 637, however, do not show any relationship between the structure of the deposit and the cathode potential. Thus over a range of p_H in the Y solution which resulted in a very great change in the crystal structure and hardness of the deposit, the cathode potential remained practically constant. This lack of relationship between crystal structure and cathode potential is consistent with results previously communicated by one of the authors. [3] It does not follow from this that the cathode potential has no influence on the character of the deposit, only that in the conditions investigated it does not exert a dominant influence, so that any broad generalisation relating crystal structure directly with cathode potential is not substantiated.

(3) Cathode Efficiency.

In all the solutions, throughout the range of p_H investigated, the cathode efficiency of nickel deposition is less than 100 per. cent., owing to the simultaneous discharge of hydrogen ions with nickel ions. This may result in (1) an effect upon the structure of the deposit caused by the discharged hydrogen, (2) an effect upon the structure of the deposit caused by nickel hydroxide or a basic salt formed in the solution adjacent to the cathode as a result of the local depletion of hydrogen ions.

(1) **Hydrogen.**—It has been suggested by various investigators that the factor which chiefly determines the structure and physical properties of electrodeposited nickel is the hydrogen which is discharged with the nickel, *e.g.*, by the formation of a nickel hydrogen solid solution, by distortion of the nickel crystal lattice or by the interference of crystal growth consequent upon the continuous formation of adsorbed films of atomic hydrogen or a surface hydride on the crystals. Thus Kohlschutter has suggested that a film of hydrogen produced on the cathode surface will make it difficult for nickel atoms to combine into even small crystals, and will hinder the development of large crystals, *i.e.*, it will fill a rôle similar to that which adsorption films of colloids exert on nickel deposits.

If this view were correct it might be expected that there would be some relationship between the amount of hydrogen discharged and the structure and physical properties of the deposit.

Within certain limits in all the solutions some degree of relationship does appear to exist. Thus in the Y solution between the limits p_H 4·7 (4·9), p_H 1·8 (2·0), in the N solution between p_H 5·3 (5·8) and p_H 1·8 (2·0) and in the F solution between the limits p_H 5·55 (6·0) and p_H 1·8 (2·0), as the hydrogen discharge increases there is an increase in the hardness of the deposit. The effect produced is a relatively small one and in all cases the rate of increase of hardness is much smaller than the rate of increase of the

amount of hydrogen discharged. This is shown in Fig. 7 for solution Y, and is typical of all three solutions, although the range is less in the F bath than in the other two baths.

It is when the relationship which exists between the cathode efficiency and the Brinell hardness number at a higher p_H range is considered, that the relative insignificance of any marked direct effect of hydrogen upon the properties of the deposit becomes apparent. Thus in the Y solution as the p_H is raised from p_H 4·7 (4·9) to 6·9 (7·1) the cathode efficiency changes from 98·8 per cent. to 99·2 per cent. i.e., the hydrogen discharge decreases

H-ion concentration (p_H quinhydrone (see page 635).
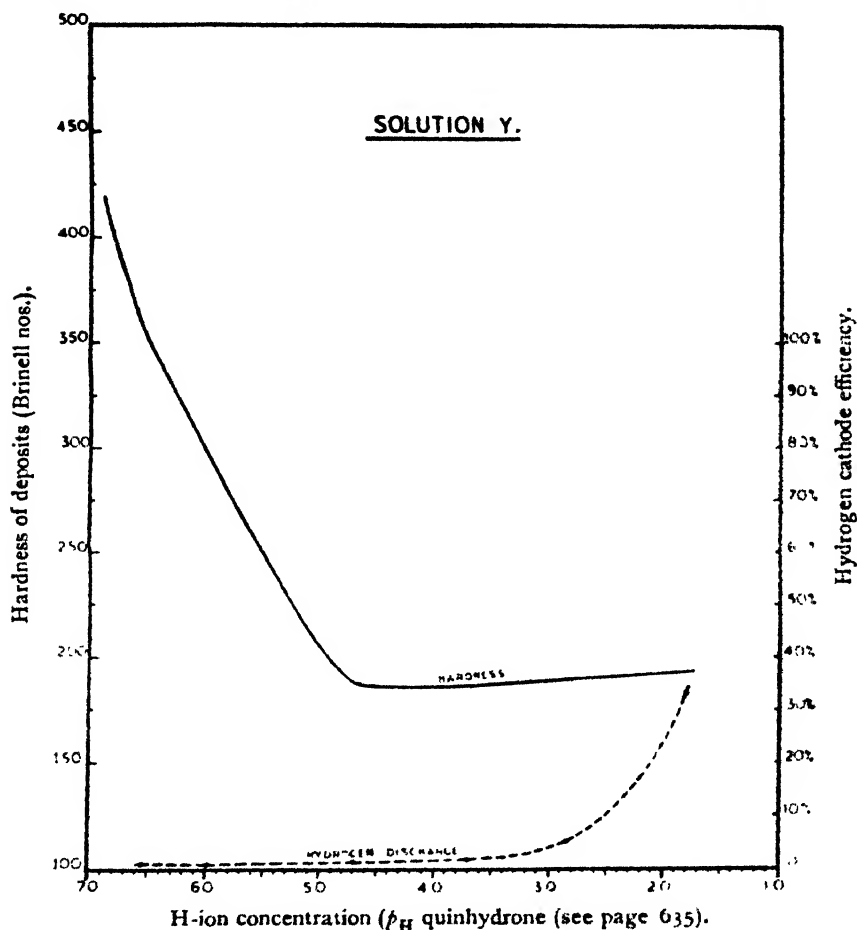
FIG. 7.

although the hardness increases from 190 to 418, and the structure of the deposits changes from a coarse to an exceedingly fine grain size.

(2) **The Formation of Nickel Hydroxide or a Basic Precipitate in the Cathode Film.**—It has been established by a number of investigations that during nickel deposition, as a consequence of the local depletion of hydrogen ions which is caused by the discharge of hydrogen, the film of liquid adjacent to the cathode is more alkaline, i.e., is at a higher p_H than the bulk of the solution. It is also well known that under certain conditions the p_H of the liquid adjacent to the cathode may rise to such a degree that nickel hydroxide or a basic salt is visibly precipitated. It has

been generally assumed that precipitation only commences under conditions that result in the production of a deposit which is dark and spongy, *i.e.*, "burnt."[12]   It has, however, been recently suggested that the formation of nickel hydroxide or a basic salt at the cathode during deposition may determine the physical properties of nickel deposits which are not "burnt."[6,7] This suggestion would appear to receive support from the results of the present investigation.

It is not possible to determine the p_H of the cathode film by any known experimental procedure so that it cannot be compared with the p_H of the bulk of the solution. Thus no direct evidence can at present be obtained as to the p_H of the bulk of the solution, at which the cathode film reaches the p_H at which precipitation of nickel hydroxide or a basic salt is known to occur. It would appear, however, that in each solution the sudden rise of hardness of the nickel deposit, with the associated refinement of structure which occurs as the p_H is raised above a certain critical value, can only be satisfactorily explained as being due to the commencement of a progressive increase in the production of nickel hydroxide or basic salt at the cathode face which, by interfering with the crystal growth, refines the structure and increases the hardness of the deposit.

If this view is correct it is to be expected that the critical p_H will be influenced by the buffer characteristics of the solution. Thus for a given rate of hydrogen discharge and under similar conditions as regards the rate at which fresh solution reaches the cathode surface (*i.e.* similar conditions of convection, diffusion, etc.) the difference between the p_H of the cathode film and that of the bulk of the solution will be largely determined by the degree to which the solution is buffered ; the less the solution is buffered the greater will be the rise in the p_H of the cathode film produced by the given rate of hydrogen discharge. In consequence the critical p_H of the bulk of the solution at which the cathode film reaches the precipitation p_H of nickel hydroxide or a basic salt might be expected to have a higher value the better the solution is buffered. The critical p_H values obtained were : F bath p_H 5·55 (6·0), N bath p_H 5·3 (5·8), Y bath p_H 4·7 (4·9). The order of magnitude of the critical p_H is thus in accordance with the relative buffer strengths of the solutions in the p_H range 4·5 to 6·0 (see Fig. 1), and is therefore consistent with the view that at the critical p_H precipitation of nickel hydroxide or basic salt occurs in the cathode film.

The progressive rise in hardness with p_H which occurs above the critical p_H (as is shown in Fig. 2) is to be expected if nickel hydroxide, or a basic salt, is the chief factor influencing the properties of the deposit. Thus there will be a tendency for nickel hydroxide or basic salt as it is formed to be redissolved in the more acid liquid continuously arriving at the cathode face. This tendency will become less as the p_H of the surrounding liquid is raised so that there will be an increase in the amount of hydroxide or basic salt available for affecting the deposit as the p_H rises above the critical p_H.

It should also follow that any differences in the rate at which nickel hydroxide or basic salt is dissolved before it affects the deposit would influence the rate of increase of hardness with rise in p_H above the critical p_H. This would appear to be of significance in explaining the more gradual slope of the p_H-hardness curve for the Y solution as compared with the N and F solutions, since there are reasons for concluding that the rate of dissolution of nickel hydroxide, or basic salt in this solution will be higher than in the other solutions. The reasons are as follows :—

(i) In the course of the work it has been found that the precipitate which

forms in the Y solution when the p_H of the whole of the solution is raised just above the precipitation point is more readily dissolved by slightly lowering the p_H of the whole of the solution than are the precipitates which similarly separate from the N and F solutions.   It appears likely therefore that in the Y solution during deposition any precipitate which forms at the cathode face will tend to be more rapidly dissolved in the liquid of lower p_H continuously arriving at the cathode surface than in the case of the other solutions.

(ii) The ammonium sulphate which is present in the Y solution functions as a buffer constituent by providing ammonium ions which interact with hydroxyl ions in the cathode film to form ammonium hydroxide. This product will tend to dissolve nickel hydroxide (or basic nickel salt) and causes its removal from the cathode face in the form of soluble complex nickel amines.   This effect is peculiar to the Y solution which alone contains ammonium salts.

It would thus appear upon comparing the results obtained in the three typical solutions that (1) the different values obtained for the critical p_H at which a progressive increase in hardness occurs, and (2) the different rates of increase in hardness with rise in p_H above the critical p_H, are consistent with the view that nickel hydroxide or a basic nickel salt is precipitated in the cathode film and affects the structure of the deposit

In a further investigation quantitative data as to the amount of nickel hydroxide or basic salt which is present in nickel deposits of differing hardness are being sought.   It does not follow however that the amount finally present in a deposit is a reliable index of the amount which originally influenced the structure of the deposit.   Thus O'Sullivan suggested as an explanation of the small amounts of oxygen found in his deposits that reduction of hydroxide (or basic salt) formed at the cathode face may have occurred due to interactions with atomic hydrogen present in the deposit whereby the amount of oxide found may be considerably less than the amount that originally affected the crystal growth of the deposit.⁷   It is also likely that the hardness and structure of the deposit may not only be influenced by the actual amount but by the physical nature of the precipitate formed at the cathode surface, e.g. a basic salt may have a greater effect on the properties of the deposit than an equal amount of nickel hydroxide.

The Possible Significance of the Hardness of Nickel Deposits as Compared with the Hardness of Annealed Nickel.

While there is a rapid increase in the hardness and refinement of structure of nickel deposits above the critical p_H in all the solutions investigated, neither at nor below the critical p_H does the hardness of the deposit reach a value which is as low as that of soft annealed nickel. Thus whereas the Brinell hardness number of the latter is about 68 the minimum Brinell hardness numbers of the deposits from the N, F and Y solutions were 160, 145 and 186 respectively.

This may be of importance in explaining the abnormal potential required for nickel deposition over a wide range [11] of p_H.   Thus, if nickel is only deposited without abnormal polarisation when it is in a fully soft condition it would appear from the foregoing that the reason why this condition is not normally obtained is that the production of soft nickel is prevented above the critical p_H primarily by the effect of nickel hydroxide or a basic salt and below the critical p_H primarily by an effect of hydrogen.   (It is

possible that above the critical p_H the effect of hydroxides or basic salts may be to some degree supplemented by that of the hydrogen which is discharged, while below the critical p_H, the effect of hydrogen may be supplemented by that of hydroxides or basic salts which may be present in the cathode film, although in smaller amounts than in the p_H range above the critical p_H.)

Summary and Conclusions.

In order to obtain further data concerning the influence of the conditions of deposition on the structure and hardness of electrodeposited nickel, deposits of this metal have been prepared in three depositing solutions in which the acidity has been varied over a wide range. The solutions were typical of those widely used in commercial practice and consisted essentially of nickel sulphate with a small proportion of potassium chloride buffered respectively with (1) ammonium sulphate (Y solution), (2) boric acid (N solution), (3) boric acid and sodium fluoride (F solution). The materials employed for the preparation of the solutions and the anodes used were specially refined and were of high purity. Deposition was carried out at a constant temperature of $35 \pm 0.5°$ C. and at a constant current density of 1·2 amp./sq. dcm. (11 amps./sq. ft.). The Brinell hardness of the deposits was determined and their micro-structure examined.

The results show that in all the three solutions the acidity exerts a very marked influence upon the hardness and structure of the deposit. In general a low acidity (high p_H) favours the formation of hard deposits having a finely crystalline structure, while a high acidity (low p_H) favours the formation of soft deposits having a larger grain size.

The hardness of the deposit was not found to increase uniformly as the p_H was raised from the lowest to the highest value employed. In each solution there was a critical p_H above which a rapid rise in hardness with p_H took place, and below which only a small change in hardness with p_H occurred.

The critical p_H values at the current density used were as follows : Y solution p_H 4·7 (4·9), N solution p_H 5·3 (5·8), F solution 5·5 (6·0).

It is thus possible by suitably adjusting the p_H of any one of the solutions to obtain hard or soft deposits. The hard deposits obtained from the N and F solutions were, however, found to contain cracks, whereas deposits of equal, or higher, hardness from the Y solution were found to be free from this defect. This confirms the previously published conclusion of one of the authors that for the production of hard deposits a nickel sulphate solution buffered with ammonium salts is the most suitable. For the production of soft deposits, at a p_H below the critical p_H, the N and F solutions, containing boric acid and sodium fluoride with boric acid respectively, appear to be more suitable, as their buffering properties are superior to those of the Y solution in this p_H range.

The possible bearing of the results obtained upon various views which have been advanced to explain the relationship of the conditions of deposition and the structure of the deposit is discussed. The conclusions reached are as follows :—

(1) The current density and cathode potential remained practically constant whether hard or soft deposits were being produced. This indicates that the structure of the deposit cannot be related directly to the intensity of the electric field of force at the cathode face which, it has been suggested, may control the crystal size of a deposit.

(2) The view that the properties of nickel deposits are largely determined by an effect on crystal growth caused by the hydrogen discharged with the nickel only receives partial support. A relationship between the amount of hydrogen discharged and the hardness of the deposit is only found to occur in a restricted range of p_H below the critical p_H, and even in this range the rise in hardness with increase in the amount of hydrogen discharged is only slight.

(3) The view that the structure of a nickel deposit may be greatly influenced by the co-deposition of nickel hydroxide or a basic salt receives strong support from the results obtained. Thus the striking rise in the hardness of the deposit which occurs as the p_H is raised above a critical p_H in all the solutions

can only be satisfactorily explained in this way. The critical p_H values in the different solutions and the rates of increase in hardness with p_H above the critical p_H are shown to be related to the buffering properties of the solutions and the solubility of nickel hydroxide or basic salt and are, therefore, consistent with this view.

The possible bearing of the results upon the abnormal potential required for nickel deposition is discussed.

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BIBLIOGRAPHY.

[1] The Hardness of Electrodeposited Iron, Nickel, Cobalt, and Copper, D. J. Macnaughtan, *J. Iron and Steel Inst.*, **109**, 409, 1924.
[2] Hardness and the Polishing of Electrodeposits, D. J. Macnaughtan and A. W. Hothersall, *J. Electroplaters' and Depositors' Tech. Soc.*, **5**, 63, 1929-1930.
[3] The Hardness of Electrodeposited Nickel, D. J. Macnaughtan and A. W. Hothersall, *Trans. Faraday Soc.*, **24**, 387, 1928.
[4] The Crystalline Form of Electrodeposited Metals, W. Blum and H. S. Rawden, *Trans. Amer. Electrochem. Soc.*, **44**, 397, 1923.
[5] The Relation between Polarisation and Structure in the Electrodeposition of Metals, V. Kohlschutter, *Trans. Amer. Electrochem. So* ., **45**, 229, 1924.
[6] The Progress of Nickel Deposition in Recent Years, D. J. Macnaughtan and R. A. F. Hammond. *J. Electroplaters' and Depositors' Tech. Soc.*, **4**, 81, 1929.
[7] Studies in the Electrodeposition of Nickel. Part I., J. B. O'Sullivan, *Trans. Faraday Soc.*, **26**, 89, 1930.
[8] " Stopping off " materials for use in the Electrodeposition of Nickel, D. J. Macnaughtan and A. W. Hothersall, *Trans. Faraday Soc.*, **26**, 163, 1930.
[9] The Measurement of p_H in Nickel Plating Solutions, W. Blum and N. Bekkedahl, *Trans. Amer. Electrochem. Soc.*, **56**, 291, 1929.
[10] The Structure of Electrolytic Copper, O. Faust, *Z. anorgan. Chemie*, **78**, 201, 1912.
[11] The Hardness of Electrodeposited Metals, R. H. Greaves, *The Metallurgist*, **1**, 141, 1925.
[12] Applied Electrochemistry. 2nd Edition, Allmand and Ellingham, p. 122.
[13] Studies of Electrolytic Polarisation. Part IV., S. Glasstone, *J.C.S.*, **128**, 2857, 1926.

THE HEATS OF DISSOCIATION OF CHLORINE MONOXIDE AND CHLORINE DIOXIDE.

By Janet I. Wallace and C. F. Goodeve.

The heat of dissociation of chlorine monoxide has been determined by several investigators, but their values differ very widely. From the heat of solution in potassium iodide, Berthelot[1] deduced a value of 15,000 calories, Thomsen[2] a value of 18,000 calories, and Neumann and Müller[3] a value of 16,000 calories. The only attempt at a direct determination was made by H. Mayer,[4] who found the heat of explosion to be 20,050 $\pm$ 1000 calories. This value has, however, been misquoted by several authorities as 23,000 calories. In our interpretation of the absorption spectrum of chlorine monoxide,[5] a rough average of the existing

[1] Berthelot, *Thermochem. Messungen*, Leipzig, 1893.
[2] J. Thomsen, *Thermochemistry*, 1908.
[3] Neumann and Müller, *Z. anorg. Chem.*, **A**, 1238, 1929.
[4] H. Mayer, *Diss.*, Hannover, 1924.
[5] Goodeve and Wallace, *Trans. Far. Soc.*, **26**, 108, 1930.

values was used, including Mayer's value as 23,000. Thus he average was considerably higher than it should have been. In view of these facts it seemed advisable to redetermine the heat of dissociation of chlorine monoxide.

The only determinations of the heat of dissociation of chlorine dioxide were those of Booth and Bowen,[6] and of Mayer.[4] Using the dioxide diluted with inactive gases, Booth and Bowen obtained a value of 23,500 calories. Mayer's value was 24,900 calories. A redetermination of this quantity was therefore undertaken.

Chlorine Monoxide.

A preliminary attempt to determine the heat of dissociation of chlorine monoxide was made by the method of Thomsen. The gas was passed directly into a calorimeter containing potassium iodide and hydrochloric acid, and the rise of temperature determined; titration of the solution showed the quantity of gas dissolved. Chlorine was passed into a similar solution, and the rise of temperature determined. The water equivalent of the calorimeter was in each case measured electrically. The heating coil for this purpose consisted of mercury contained in fine-drawn pyrex capillary tubing, through which a current could be passed. The values obtained averaged about 18,000 calories, but the limits of error were greatly magnified in the calculations, since the heat of dissociation of chlorine monoxide is finally obtained as the difference between two very large quantities. This method was therefore abandoned in favour of a direct determination of the heat of explosion.

For both methods, chlorine monoxide was prepared by passing a mixture of chlorine and air through a reaction vessel containing mercuric oxide (freshly precipitated and heated to 200° for one hour), mixed with sand. The gas was condensed in a CO_2-alcohol mixture, passed through P_2O_5, and through freshly precipitated unheated mercuric oxide to free from chlorine, and finally was fractionated three times. Samples for analysis were condensed in small tubes surrounded by liquid air, and the tubes sealed off. They were then cut off and dropped into concentrated solutions of potassium iodide, containing a known quantity of standard HCl. The iodine liberated according to the equation:

$$Cl_2O + 4KI + 2HCl \rightarrow 4KCl + H_2O + 2I_2$$
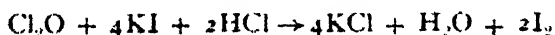
is titrated with sodium thiosulphate, and excess the HCl with NaOH. The ratio of thiosulphate to HCl is a measure of the purity of the chlorine monoxide.

Apparatus.—The calorimeter consists of a large "Thermos" Dewar vessel, supported in a copper vessel filled with water. (Fig. 1). In the Dewar vessel are supported the explosion chamber A, the stirrer C, and the heating coil H. The temperature is measured on a standard Beckmann thermometer. The heating coil consists of fine nichrome wire wound on mica, and the current and voltage across it are measured with instruments standardised against a Weston cell. The stirrer C is operated at a constant rate by a small electric motor. The explosion chamber is in the form of a U-tube of thin-walled glass-tubing, about 8 cm. long and 1 cm. in diameter, closed at one end. The other end connects through a three-way tap to the source of supply of Cl_2O on one side, and to the high vacuum

[6] Booth and Bowen, *J. Chem. Soc.*, 342, 1925.

pump on the other.   Two platinum wires are sealed in at the bottom of
the tube to give a very small spark gap.   The tap is rotated by a spring
motor turning the pulley F.   E is a shaft consisting of two small universal
joints, since it was impossible to obtain a tap which was sufficiently true to
use a rigid shaft.   The tap is lubricated with chlorinated vaseline, which
was the only satisfactory substance of many which were tried.   G is a liquid
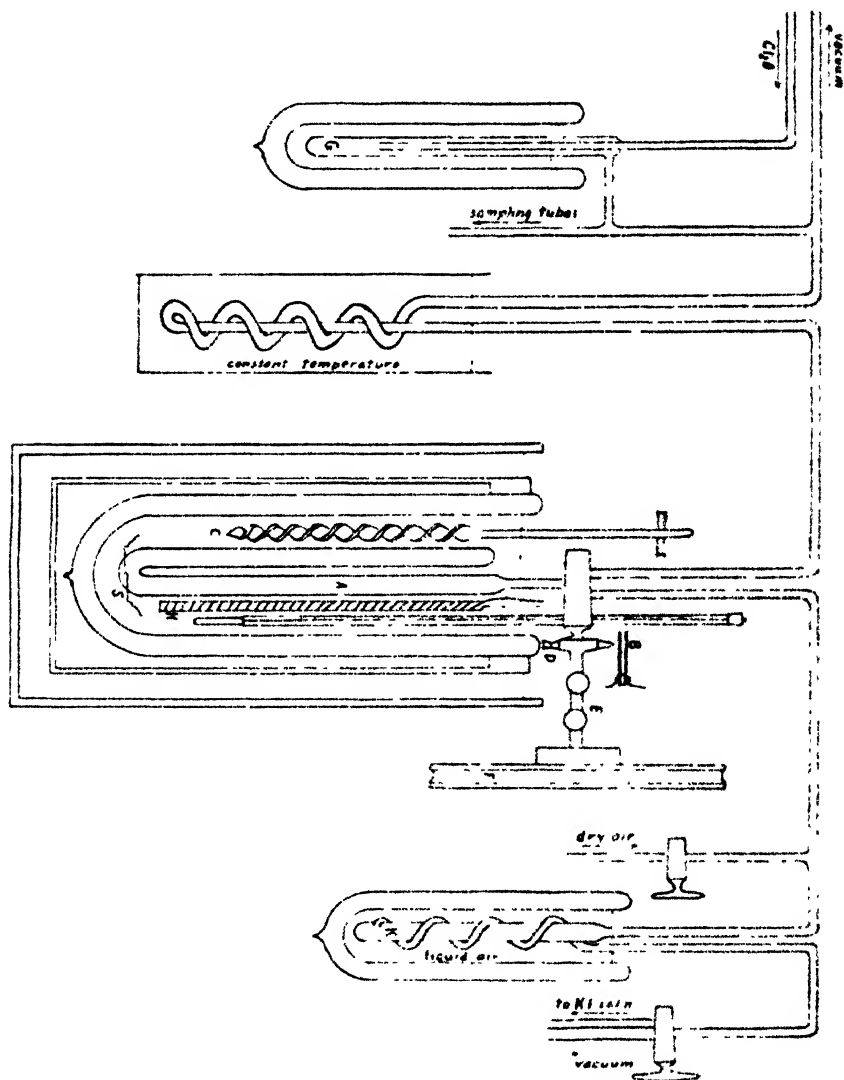
FIG. 1.

air trap containing the purified Cl_2O.   Between G and the calorimeter the
gas passes through a long spiral immersed in water at the temperature of
the calorimeter, to ensure that the gas is at the temperature of the calori-
meter before entering the explosion chamber.   K is also a liquid air-trap,
in which the chlorine resulting from the explosion is condensed.   The
calorimeter is filled with B.P. paraffin, on account of its low specific heat
and high insulating properties.

Procedure.—The calorimeter liquid is stirred and the temperature is read every minute for a period of twenty to thirty minutes, when the rise of temperature with time has become quite linear. The heating effect of the stirring in this calorimeter is considerable. A current is then passed through the heating coil (current, voltage, and time being accurately measured), for about thirty seconds, and the temperature again read every minute for twenty to thirty minutes. The liquid chlorine monoxide is warmed to room temperature, and the explosion chamber and trap K are evacuated by a high vacuum pump. Rotation of the tap is then begun. When A is opened to G, chlorine monoxide rushes into the evacuated chamber A. As the tap turns, the chlorine monoxide supply is cut off, and the end of the tap D then closes a small switch B, which causes a spark to pass in the Cl₂O, exploding it. Further rotation of the tap allows the products to be drawn off by the pumps, the chlorine being condensed in the
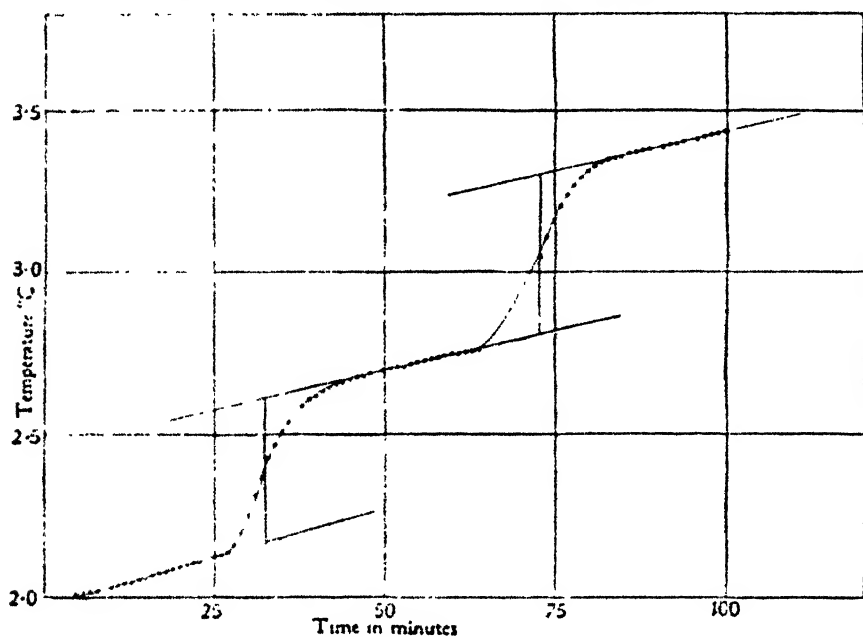
Fig. 2.

trap K. The cycle is repeated with each rotation of the tap. The number of explosions varied for different experiments, but was usually about fifteen. The speed of rotation of the tap also varied for different experiments. During the explosions, and for twenty to thirty minutes after, the temperature was read every minute as before. The temperature readings are plotted as a function of the time, and the time-temperature curves so obtained give, on extrapolation (Fig. 2) a true measure of the rise in temperature due to the heating coil and to the explosions. The rise in temperature was usually about $0.5°$ C., and the heat equivalent of the calorimeter about 340 calories per degree rise in temperature. The experiments were carried out at room temperature.

The chlorine condensed in K is driven into a solution of potassium iodide and hydrochloric acid by means of a current of dry air. The solution is titrated as before, the amount of HCl used indicating any undecomposed chlorine monoxide. Knowing now the purity of the original gas,

and the amount of chlorine resulting from its decomposition, the amount of chlorine monoxide exploded may be calculated. Knowing also the quantity of heat developed by these explosions, the heat of dissociation of one gram-molecule may be calculated. Table I. gives a summary of six determinations of the heat of dissociation (at constant volume) of chlorine monoxide. A mean value of 21,735 ± 560 calories is obtained.[7]

<div align="center">TABLE I.</div>

Amount of Cl_2O. (Gms.)	Temp, Increase. (°C.)	Heat Equiv. of Calorimeter. (Cals. per Degree.)	Heat of Diss. (Cals. Per Gm. Mol.)
·4171	·357	290·1	21,580
·6563	·505	332·7	22,250
·6422	·542	286·7	21,030
·7861	·554	342·1	20,950
·7027	·493	364·1	22,200
·4850	·377	331·5	22,400
		Mean . . .	21,735 calories.
		Probable error .	± 560 ,,

Possible constant sources of error were carefully checked. The tap was rotated at various speeds, giving from two to fifteen explosions per minute, and since this did not alter the results, it was concluded that all the heat of the explosions was absorbed in the calorimeter. To ensure that all the chlorine products were absorbed in the KI, a second bubbler of KI was placed in series with the first, and in addition, when the reaction appeared to be complete, a fresh bubbler was substituted for the first, and the air passed through for twenty minutes or more. The heating effect of the spark was tested, and was found to be quite undetectable. The apparatus was painted black to exclude the possibility of photochemical decomposition. The purity of the remaining undecomposed gas was usually determined at the end of the experiment, but the Cl_2O was never found to have undergone more than very slight thermal decompostion.

Chlorine Dioxide.

The method of determination of the heat of dissociation of chlorine dioxide followed closely that of the monoxide.

The chlorine dioxide was prepared by addition of concentrated sulphuric acid to potassium chlorate, cooled with CO_2 alcohol. The gas is dried with P_2O_5 and fractionated three times. It is analysed in the same manner as the monoxide, the equation being :

$$2ClO_2 + 10KI + 8HCl \rightarrow 10\ KCl + 4H_2O + 5I_2.$$
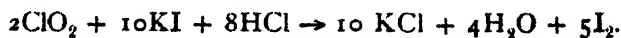
The apparatus is also essentially the same as for chlorine monoxide. A slightly different form of explosion chamber was used, consisting of a

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[7] Since writing this paper, a paper by Gunther and Wekua has appeared (*Z. physik. Chem.*, A, April, 1931) in which the heat of dissociation of chlorine monoxide was determined as 25,099 ± 100 cals. The discrepancy between their results and these here recorded is not easily accounted for. The total heat developed in their experiments was about six calories, while in ours it was fifty to sixty times as great. Consequently their variable correction of from one to fifteen per cent., due evidently to loss or gain of heat from the surroundings and to the stirrer is large in view of the small amount of heat developed by the explosion. Also the method of analysis has not apparently been tested in any way. The solution of a very small amount of oxygen in the NaOH and hypochlorite solution would account for the difference in our results.

U-tube as before, but having a second U-tube of 5 mm. thin-walled glass inserted between the original U-tube and the tap, thus giving a much larger surface for the heat transfer. The procedure is identical with that described above, except that much lower pressures of chlorine dioxide had to be used, due to its detonating power. The liquid chlorine dioxide was kept in a freezing mixture of ice and salt during the explosions, so that the pressure of chlorine dioxide in the explosion chamber would be about 250 mm. The number of explosions was correspondingly increased. Also, since the explosion was accompanied by a bright flash of light, the calorimeter liquid was stained with dye to absorb the light. The results, however, were not different, with and without this dye. The results are given in Table II.

TABLE II.

Amount of ClO₂. (Gms.)	Temp. Increase. (° C.)	Heat Equiv. of Calorimeter. (Cals. Per Degree.)	Heat of Diss. (Cals. Per Gm. Mol.)
·6136	·731	329·7	26,500
·4030	·472	335·6	26,520
·4559	·556	335·6	27,610
·2733	·312	334·4	25,760
·5958	·704	331·1	26,400
·4930	·560	348·7	26 720
		Mean . .	26,585 calories.
		Probable error .	± 390 ,,

A small error seems to be inherent in the method of analysis. Other sources of error were checked as for chlorine monoxide, and the results for the two gases have about the same limits of error.

Stability of Cl₂O and ClO₂.—Several interesting properties of chlorine monoxide were observed during the course of these experiments. The observed stability is particularly surprising in view of the oft-repeated statements as to the violently explosive character of this gas. It was found that when the gas was pure, or contaminated with relatively small quantities of chlorine, no explosion could be obtained unless the pressure of the gas was atmospheric or greater. When the spark was passed in the gas at low pressures, a bluish glow appeared around the electrodes and spread for a short distance in their neighborhood. Reaction chains apparently exist, but are not propagated far at low pressures. On the other hand, when the chlorine monoxide was illuminated for a few minutes with a 100-candle power "Pointolite," the explosion at low pressure was so violent as to shatter the apparatus.

The relative stabilities of chlorine monoxide and chlorine dioxide were tested in several ways. Chlorine dioxide may undergo continuous decomposition by a process resembling a flame. A fine jet from which the gas is issuing may be lighted with a match, giving a bluish white light. In most circumstances this "flame" travels back to the source of supply and detonates it. Chlorine monoxide cannot be ignited in this way. Again, when a tube containing liquid or solid chlorine dioxide is dropped on a cement floor, it detonates violently even at − 100° C. On the other hand, liquid chlorine monoxide at room temperature does not detonate when dropped from a great height.

These facts do not appear to be compatible with Hinshelwood's [b] views

[b] Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, p. 64, 1929.

that the thermal decomposition of Cl_2O is a bimolecular reaction requiring a heat of activation of 22,000 calories. If two molecules collided, having the required heat of activation, their decomposition would liberate 43,500 calories. The total heat available for the three separating molecules would then be 65,500 calories. If this is equally divided, each molecule would then possess almost 22,000 calories, the heat of activation. Under these circumstances, a reaction chain once started would propagate instantly throughout the gas, resulting in immediate violent explosion. The decrease in the stability of the chlorine monoxide on illumination, as opposed to its stability under ordinary circumstances, apparently points to the formation of an intermediate product of decomposition. This gives support to the view of Beaver and Stieger [9] that the thermal decomposition is not a bimolecular reaction, but a chain reaction involving the formation of an intermediate product.

Summary.

The heats of dissociation of chlorine monoxide and chlorine dioxide have been determined by a direct measurement of the heat of explosion, as $21,735 \pm 560$ calories and $26,585 \pm 390$ calories respectively. An apparatus has been described in which a series of explosions, giving a temperature rise of about half a degree Centigrade, may safely take place. Some interesting properties of chlorine monoxide and chlorine dioxide have been discussed, with particular reference to the thermal decomposition of chlorine monoxide and the relative stabilities of chlorine monoxide and chlorine dioxide.

[9] Beaver and Stieger, *Z. physik. Chem.*, B. 12, 93, 1931.

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THE ADSORPTION OF HYDROGEN BY A ZINC OXIDE-CHROMIUM OXIDE CATALYST.

By F. E. T. Kingman.

In an earlier communication it has been shown [1] that the adsorption of carbon monoxide and hydrogen by a zinc oxide-chromium oxide catalyst presents several interesting features.

It was shown that carbon monoxide or hydrogen, adsorbed at room temperatures at equilibrium pressures of 10^{-3} to 10^{-4} cm., is evolved on heating the catalyst to 100-126° C. but is rapidly readsorbed at a rate which increases with rise in temperature. On raising the temperature still further, no more gas is evolved until, at 350° C, either carbon dioxide or water is liberated. These results were shown by H. S. Taylor [2] to be in agreement with his theory of the activation energy of adsorption processes.

The work has been continued and a detailed study has been made of the adsorption of hydrogen on the zinc oxide-chromium oxide catalyst at − 80° C., 0° C. and 100° C. The freshly prepared or oxidised catalyst

[1] Garner and Kingman, *Nature*, 126, 352, 1930; *Trans. Faraday Soc.*, 27, 322, 1931.
[2] *J.A.C.S.*, 53, 578, 1931.

undergoes reduction on repeated treatment with hydrogen, and the rates of adsorption of hydrogen have been measured on the catalyst at various stages in the reduction.

Apparatus.

10·76 gm. of the catalyst were contained in a Pyrex bulb, connected by means of a Pyrex-soft glass ground joint to a McLeod gauge and gas burette. The catalyst was activated by heating the bulb by a small electrical furnace to 440° C. under a high vacuum. The bulb was surrounded by solid CO_2 and methylated spirits, melting ice and steam for experiments at − 80° C., 0° C., and 100° C. respectively.

The system could be evacuated either by a Gaede steel diffusion pump backed by a "Cenco" Hyvac oil pump, or by a Toepler pump; the use of the latter made it possible to collect the hydrogen evolved during the activation process, water vapour being removed by a phosphorus pentoxide tube.

Before each experiment the catalyst was activated for at least two hours, then immersed in the appropriate constant temperature bath and left for $1\frac{1}{2}$ to 2 hours to acquire a steady temperature. 1·7 c.c. of hydrogen were then admitted and pressure readings on the McLeod gauge taken at regular intervals. From the value of the residual pressure (the volume of the system being known from a previous calibration with helium) the volume of gas unadsorbed, and hence the volume adsorbed, could be calculated.

Two preliminary series of experiments were carried out on the fully oxidised catalyst (Table I., Series A, B and C). In these experiments it was found that all the hydrogen which was adsorbed could not be removed as such on raising the temperature, i.e. some reduction of the catalyst had taken place, and the gas not removed as hydrogen must have been oxidised, in agreement with the earlier observations on this catalyst.[1]

TABLE I.

Expt. No.	Temperature of Experiment. ° C.	Volume of Hydrogen Adsorbed (c.c.) at			
		0·05 Hours.	0·60 Hours.	1·00 Hours.	5·00 Hours.
Series A.					
1	0	0·080	0·158	0·196	0·270
2		0·070	0·153	0·178	0·263
3		0·078	0·162	0·188	0·295
4		0·109	0·190	0·212	0·335
Series B.					
4	0	0·307	0·510	0·565	0·740
5		0·471	0·750	0·810	1·015
7		0·528	0·830	0·890	1·100
9		0·533	0·833	0·895	1·100
12		0·590	0·900	0·970	1·185
Series C.					
1	100	0·658	1·301	1·438	1·692
3		0·581	0·975	1·067	1·370
6		0·784	1·090	1·150	1·295
8		0·788	1·095	1·150	1·300
10		0·787	1·095	1·145	1·290
11		0·849	1·164	1·219	1·365

It will be seen that on reduction of the catalyst, a slight decrease in adsorptive power took place, followed on further reduction by a very definite increase. The catalyst was oxidised afresh and a further series carried out at 0° C. (Series B) and 100° C. (Series C).

The catalyst was strongly reduced by allowing hydrogen to remain in contact with the catalyst at 300° C. between 1 and 3 and at 340° C. between 4 and 5 and again at the same temperature between 10 and 11. Considerable reduction of the catalyst had thus occurred before the first experiment at 0° C. was carried out.

The adsorptive capacity at 100° C. is first of all decreased and then later increased by the reduction of the catalyst. Between experiments 7 and 10 the adsorptive capacity of the catalyst is practically constant.

No measurements were made of the amount of reduction of the catalyst surface in the above experiments. It was desirable to do this, so the catalyst was reoxidised and a fresh series commenced. In this series the volumes of hydrogen admitted to the catalyst, and the volumes removed as such on activation were carefully measured. The difference between the volume admitted and that removed was assumed to be the volume of water produced by the reduction of the catalyst, and was used as the measure of the extent to which the catalyst had been reduced.

TABLE II.

Series D.

Expt. No.	Temperature of Experiment. °C.	Hydrogen Used up. c.c.	Volume of Hydrogen Adsorbed (c.c.) at			
			0·05 Hour.	0·60 Hour.	1·00 Hour.	5·00 Hours.
16	− 80	63·7	0·495	0·666	0·763	0·840
19		67·0	0·536	0·740	0·835	0·920
22		69·4	0·535	0·735	0·810	0·880
1	0	0·0	0·229	0·385	0·485	0·575
3		2·24	0·162	0·285	0·355	0·430
6		6·42	0·115	0·220	0·315	0·385
9		26·8	0·263	0·423	0·510	0·590
11		43·0	0·274	0·440	0·540	0·620
13		46·4	0·298	0·472	0·575	0·670
14		62·5	0·347	0·580	0·710	0·830
17		66·5	0·449	0·737	0·880	0·997
21		69·4	0·549	0·803	0·960	1·080

TABLE III.

(Series D continued)

Expt. No.	Temperature of Experiment. °C.	Hydrogen Used up. c.c.	Volume of Hydrogen Adsorbed (c.c.) at			
			0·05 Hour.	0·40 Hour.	1·00 Hour.	4·00 Hours.
2	100	0·56	0·491	0·920	1·283	1·640
4		3·02	0·358	0·746	1·090	1·535
7		8·13	0·303	0·643	0·959	1·380
10		27·1	0·422	0·587	0·706	0·865
12		44·7	0·413	0·548	0·630	0·720
15		63·2	0·617	0·810	0·930	1·050
18		66·8	0·718	0·945	1·072	1·190
20		69·0	0·758	0·980	1·100	1·230

The volume of hydrogen used up (given in the third column) is the volume of gas which previous to the experiment had been admitted to the catalyst and had not been pumped off as hydrogen.

The results for o° C. are shown in Fig. 1a, the volume of hydrogen adsorbed at 0·05, 0·60, 1·00 and 5·00 hours being plotted against the reduction of the catalyst (as measured by the volume of hydrogen used up) in curves I., II., III. and IV. respectively. These curves show a minimum at a reduction of 6 c.c. after which the rate of adsorption rises to a flat maximum at 30-40 c.c. reduction, and then with subsequent reduction rises more steeply.

The results for 100° C. at 0·05, 0·30, 1·00 and 4·00 hours are shown similarly in Fig. 1b, curves I., II., III. and IV. respectively. These curves are simpler in form than those for o° C., and in most cases show a simple minimum at 40 c.c. reduction. Curve I. however is similar in form to the

(a)   (b)
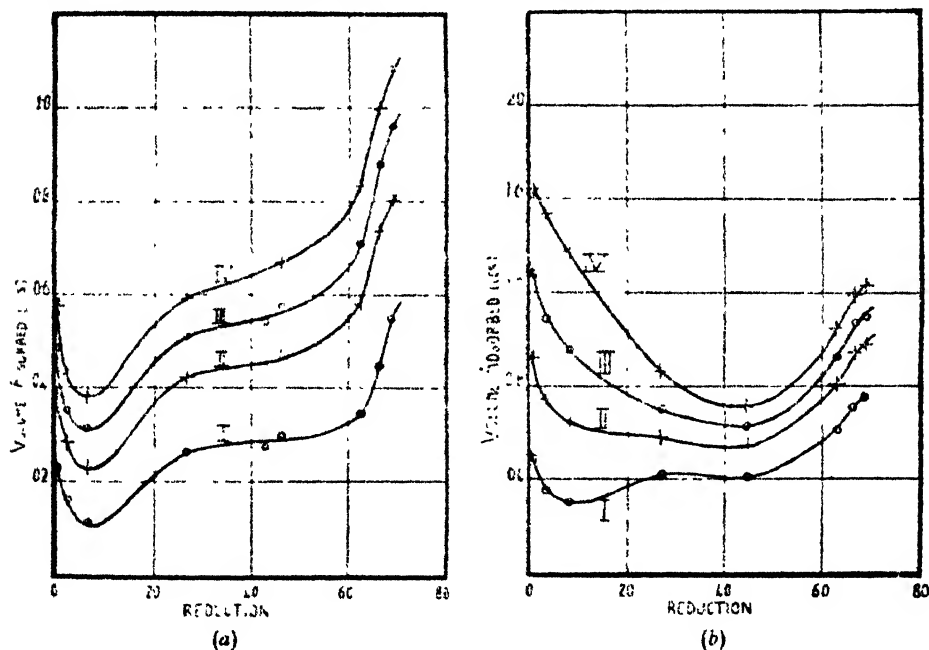
Fig. 1.

curves for o° C. showing a minimum at 8 c.c. and a flat maximum at 25-45 c.c. reduction.

The results for the three series A, B and D are practically identical in so far as they can be compared, except for a slight decrease in adsorptive power which occurs, probably as a result of the oxidation process, between B, and D.

Attempts were made to analyse the rates of adsorption in order to determine if they obeyed any simple law. These attempts were not successful except in the case of two experiments at o° C., A. 4, and D. 3, which were continued for 165 and 140 hours respectively. In these two experiments it was found that after the first thirty hours, the rate of adsorption could be accurately represented by the equation,

$$\frac{dx}{dt} = kp^2.$$

As will be shown later there are probably three different types of adsorption occurring over a narrow temperature range.   In view of this highly complex nature of the adsorption process, it was not to be expected that any simpler relationship would fit the whole adsorption curve.
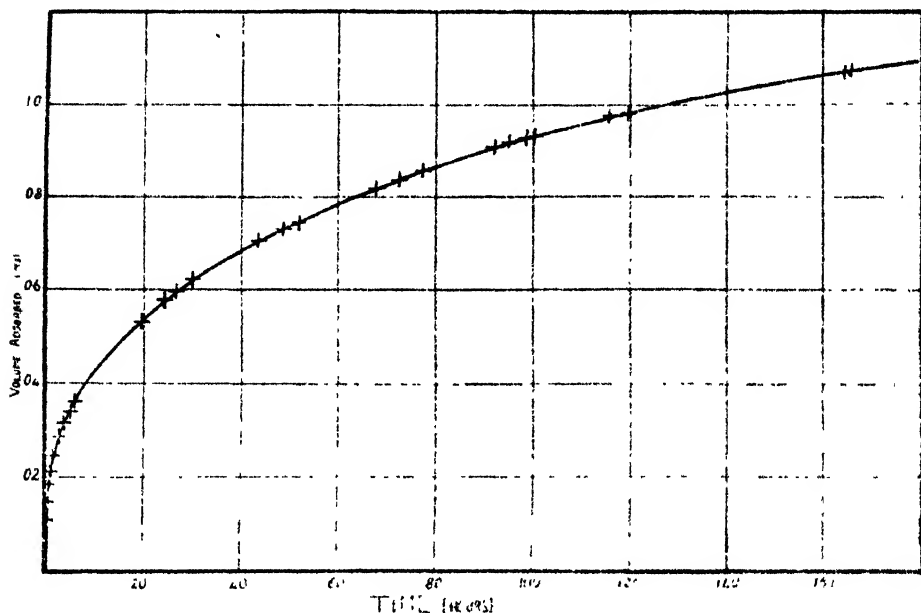
FIG. 2.—Expt. A 4.   Temperature of experiment = 0° C.
Duration of experiment = 165 hours.

Curves showing the amount adsorbed plotted against time for individual experiments are shown in Figs. 2 and 3.   The experiments to which these curves refer are given below.

Discussion.

The curves in Fig. 1 show that as the catalyst is reduced the total rate of adsorption first falls and then increases.   Further, it has been demonstrated that the quantity of hydrogen adsorbed irreversibly and removable only as water decreases when the catalyst is reduced.   The initial fall in adsorption must therefore be due to a decrease in the reducible area of the surface and may possibly be ascribed to the removal of the most active of these centres.   As these centres are removed, they are replaced by others, which can still adsorb hydrogen without further reduction of the surface. Thus, adsorption takes place on two types of area, *viz.* the oxygen atoms of the surface, and the reduced centres.   As adsorption on the former decreases, that on the latter will increase.

The minimum can be accounted for as due to the superposition of two curves, (*a*) that for the rate of adsorption on the oxidised centres, and (*b*) that for the rate of adsorption on the reduced centres.   The first curve falls off rapidly, because the more active oxygen atoms are removed first. It can be shown that the rate of adsorption on the reduced centres must rise rapidly with reduction of the surface.   The greater the forces holding an oxygen atom to the surface, the more slowly will it adsorb hydrogen molecules.   If, however, one of these strongly held oxygen atoms be

removed by reduction, the reduced centre produced will be expected to possess a very high potential energy and therefore will be very reactive. It therefore follows that the activity of the reduced centres increases as the reduction proceeds. The rate of adsorption on the reduced centres depends on their activity, and hence the rate of adsorption on these centres must increase as the catalyst is progressively reduced. Thus the rapid increase in the rate of adsorption as the reduction of the catalyst reaches
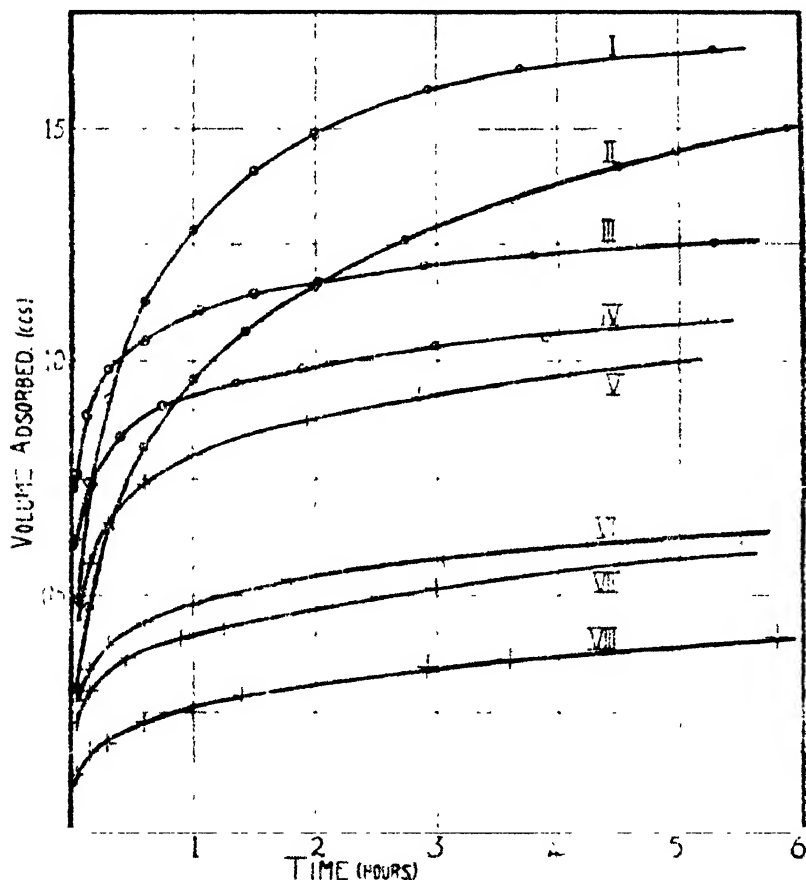
Fig. 3.

Curve No.	Expt. No.	Curve No.	Expt. No.
I.	D. 2	V.	D. 17
II.	D. 7	VI.	D. 11
III.	D. 20	VII.	D. 1
IV.	D. 15	VIII.	D. 6
Tempr. of expts. = 100° C.		Tempr. of expts. = 0° C.	

its conclusion can be explained as due to the increase in the activity of the reduced centres. On account of the complexity of the adsorption process it does not appear possible to give a quantitative explanation at the present time.*

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* The curves at 0° C. are more complex than those at 100° C. In order to explain these curves it is necessary to assume the presence of two types of reduced centres, or two successive steps in the reduction.

The results described in the experimental part of this paper indicate that there are three types of adsorption of hydrogen on the zinc oxide-chromium oxide catalyst :—

(1) A Van der Waals type of adsorption, which occurs at low temperatures, with a low heat of activation. This type is greater at − 80° C. than at 0° C.

(2) Another adsorption process which possesses an appreciable heat of activation, and a heat of adsorption of 20-30 Cal. The rate of this type of adsorption increases with temperature.

(3) A process by which the hydrogen is irreversibly attached to the surface and can only be removed on subsequent heating as water. It occurs at an appreciable rate only at 100° C. and on an oxidised surface. As the catalyst is reduced this type of adsorption disappears, as is shown by the fact that on the reduced catalyst all the adsorbed hydrogen can be recovered as such.

The results obtained by Taylor and Williamson,[3] for the adsorption of hydrogen on a manganous-chromium oxide catalyst provide a clear example of types I. and II. Adsorption below 0° C. takes place with a low heat of activation, whereas above 0° C. a very slow process of adsorption occurs with a high heat of activation ; furthermore, the total adsorption is much greater at 305° C. than at − 78° C. No reduction of the catalyst takes place, the hydrogen being removable as such at 460° C.

In the present experiments, in addition to types I. and II., there is a third type which results in the chemical combination of the hydrogen with the oxygen atoms of the surface and, on desorption, the catalyst is reduced. These three types occur over such a narrow range of temperatures that it is difficult to separate their effects. Type III. (i.e. chemisorption) only occurs at an appreciable rate at 100° C. ; at 0° C. there may be some chemisorption on the more active centres, but from the amount of hydrogen given up on raising the temperature to 100° C., it must be very small. Nevertheless, the possibility of the occurrence of some chemisorption at 0° C. makes it difficult to distinguish clearly the existence of the three types of adsorption on the oxidised catalyst.

Reduced Catalyst.

When the catalyst is nearly reduced, the figures shown in Table IV. were obtained for the amounts of adsorption after 3 minutes and 4 hours

TABLE IV.

Temperature, °C.	Hydrogen Used up. c.c.	Volume Adsorbed at	
		3 Mins. c.c.	4 Hours. c.c.
− 80	63·7	0·495	0·840
0	66·5	0·449	0·997
100	66·8	0·718	1·190
− 80	67·0	0·536	0·920
100	69·0	0·758	1·230
0	69·4	0·549	1·080
− 80	69·4	0·535	0·880

[3] *J.A.C.S.*, **53**, 2168, 1931.

for − 80° C., o° C. and 100° C. It will be seen that the figures are in both cases higher for 100° C., than for either o° C. or − 80° C. This holds for both the rapid and the subsequent slow adsorption, when the catalyst has been completely reduced. This increase in adsorption with increase with temperature must correspond to a transition region between two types of adsorption (cf. Taylor).[2] Neither of these two types can include chemisorption since the catalyst is completely reduced. Therefore the two types must be similar to those found by Taylor and Williamson [3] for manganous-chromium oxide.

The amounts of adsorption after three minutes, are not very different for o° C. and − 80° C; after 4 hours, however, the amount of adsorption is decidedly larger at o° C. than at − 80° C. If the adsorption in the first few minutes is mainly the rapid adsorption of hydrogen without activation energy (i.e. of the Van der Waals type) and the subsequent slow adsorption that occurring with an appreciable energy (i.e. type II.), then these results are intelligible.

It is therefore concluded that in the adsorption of hydrogen on a zinc oxide-chromium oxide catalyst all three types of adsorption are present.

Summary.

1. The adsorption of hydrogen on a zinc oxide-chromium oxide catalyst has been studied at − 80° C., o° C. and 100 C The variation in the rates of adsorption with reduction of the catalyst has also been investigated.

2. It has been shown that the adsorption process is highly complex owing to the occurrence of three distinct types of adsorption :—

    I. Van der Waals adsorption ;

    II. adsorption with a high heat of activation, but not leading to the reduction of the catalyst ;

    III. adsorption on the oxygen atoms of the surface leading to reduction of the catalyst.

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THROWING POWER OF PLATING SOLUTIONS WITH PARTICULAR REFERENCE TO CERTAIN ZINC PLATING SOLUTIONS.

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This work was undertaken as part of a general investigation of the electrodeposition of metals upon aluminium and aluminium alloys with special reference to the protection of aluminium or its alloys against corrosion. The work forms part of a research in progress for the Electrodeposition Committee of the Department of Scientific and Industrial Research.

The method used for determination of "Throwing Power" in this

work was that devised by Haring and Blum.[1] As a general definition Haring and Blum state that "throwing power" is "that property of a solution by virtue of which relatively uniform distribution of metal is obtained upon a cathode of irregular shape." If an irregularly shaped cathode is immersed in a plating bath and two small equal areas of its surface are considered, one of which is nearer to the anode than the other, the resistances through the solution from the anode to the two areas are inversely proportional to the respective current densities on the two areas provided that there is no polarisation. This condition could be approximately realised by the use of high frequency alternating current. The ratio of these hypothetical current densities, known as the "Primary Current Ratio," is dependent entirely on the arrangement of anode and cathode and the shape and size of the containing vessel and is independent of the composition of the electrolyte.

In many plating baths a direct current produces polarisation of the cathode which increases with the current density. This reduces the current density on the more polarised part of the cathode and in consequence the "actual" or "Secondary Current Ratio" becomes more nearly unity than the primary current ratio.

The ratio of weights of metal deposited on the two areas of the cathode under consideration is known as the "Metal Distribution Ratio" or simply as the "Metal Ratio." This is the same as the secondary current ratio only if the cathode current efficiency is the same at the two current densities concerned. This condition is not at all common and it is necessary to distinguish between the secondary current ratio and the metal ratio.

A numerical value for throwing power can be deduced and is defined as follows :—

The "Throwing Power" of a solution is the deviation of the metal distribution ratio from the primary current distribution ratio and is generally expressed as a percentage of the primary current distribution ratio.

Thus if $K : 1$ is the primary current ratio where K is greater than unity, and $M : 1$ is the corresponding metal distribution ratio,

then the throwing power $= \dfrac{(K - M)\,100}{K}$ per cent.

From this formula it is evident that a negative throwing power is possible and would signify that less metal had been deposited on the more distant part of the cathode than would be expected from the primary current ratio.

The factors which govern the throwing power of a solution are :—

(a) The slope of the deposition potential-current density curve between the values of the current density on the near and far parts of the cathode. This represents the excess polarisation of the part near the anode over that of the part remote from the anode and is generally the chief factor producing a good throwing power.

(b) *Conductivity of the Plating Bath.*—If the conductivity of the bath is high the voltage drop through the solution for any given current density will be relatively low and its ratio to the difference of polarisation on the two areas of the cathode under consideration will be small. If, however, the conductivity is low the voltage drop through the solution at the same current density will be high and will reduce to a large extent the beneficial effect of differential polarisation.

(c) *Cathode Current Efficiency.*—This frequently varies with the current

density and so will modify the effect of polarisation. It may assist or may be detrimental to the production of a good throwing power.

Throwing Efficiency.

A method of reporting the results of throwing power has been suggested by Heatley, and he calls his final value "throwing efficiency." The objection to the throwing power function as already defined is that with a perfect solution which gives even distribution of deposit however great the primary current ratio, the throwing power value is never 100 per cent. but increases from zero with a primary current ratio of 1 : 1 and approaches 100 per cent. asymptotically. Throwing efficiency is defined as "the amount of actual improvement of metal distribution ratio over primary current distribution, in comparison with ideal improvement based on perfectly uniform deposit over all parts of the cathode."

$$\text{Throwing efficiency} = \frac{\text{Actual throwing power}}{\text{Ideal throwing power}} \times 100 \text{ per cent.}$$

Where the "Ideal throwing power" indicates a metal ratio (M) of 1 : 1.

$$\text{Throwing efficiency} = \frac{\dfrac{(K - M) \times 100}{K}}{\dfrac{(K - 1) \times 100}{K}} \times 100 \text{ per cent.}$$

$$= \frac{K - M}{K - 1} \times 100 \text{ per cent.}$$

If the throwing efficiency were a fixed value for each bath, independent of primary current ratio, a great advantage would be gained. However, L. C. Pan [2] has determined and plotted the throwing power and the throwing efficiency for three plating baths. None of the throwing efficiency curves differs very greatly from or is appreciably more constant than, the corresponding throwing power curve.

It is considered, therefore, that the advantage of reporting results as throwing efficiency is counterbalanced by the slightly greater complexity of the throwing efficiency function compared with the throwing power function and so results have been published as throwing powers in this paper.

Many methods have been devised for determining throwing power, but up to date the author has seen none that is capable of giving results that have a mathematical significance which is capable of being readily correlated with the electro-chemical properties of a plating bath, viz., polarisation, conductivity, and current efficiency, except that devised by Haring and Blum.[1]

Description of Apparatus.

The container for the plating bath under test was a rectangular ebonite box 60 cm. × 10 cm. × 13·5 cm. deep. A line was scored round the inside of the box 10 cm. from the bottom to serve as a mark to which the box should be filled when in use. Slots 0·15 cm. wide by 0·15 cm. deep were cut vertically in the sides every 5 cm. of the length of the box and into these the anode or cathode plates could slide.

The anode consisted of a plate of high purity "Australasian Electrolytic Zinc" 10·2 cm. × 14 cm. perforated by 99 holes ⅛ in. diameter in order to keep both sides as nearly as possible at the same electrode potential during

[1] *Trans. Amer. Electrochem. Soc.*, **58**, 255, 1930.

electrolysis.   Haring and Blum[1] used wire gauze for their experiments, but pure zinc wire gauze was not readily available.   For the first experiments a cast zinc anode was used and for later work the anodes were made of rolled sheet.

The cathode consisted of 20 gauge sheet material and was in two parts each 10·2 cm. × 14 cm. connected externally to the bath by a heavy copper conductor.   For most of the work duralumin cathodes were used.   In addition tests were made with aluminium, commercial zinc, copper, brass and mild steel cathodes.   The cathodes were prepared by lightly sandblasting them on the side to be plated.   For this, fine sand was used and the air pressure was regulated to approximately 10 lb. per square inch.   Any dust remaining on the surface was removed with a camel hair brush.

When a test was made, the two half cathodes were weighed after brushing and standing in a dessicator over calcium chloride for a short time. Binding screws were passed through holes in the top of each half cathode and were screwed up securely.   The binding screws were connected by a heavy copper wire.   The anode was slid into a suitable pair of slots in the walls of the box, and after electrical connections had been made the two half cathodes were slid into slots on either side of the anode so that the distances from the half cathodes to the anode were in an inverse ratio as the desired primary current ratio.   Suitable rheostats and ammeter were in series with the bath and the current flow was adjusted at once so as to give the desired average current density.

After electrolysis had continued for the period of the test, the two half cathodes were removed from the bath before the current was switched off and were washed, finally with distilled water, dried rapidly in a current of air, dessicated and again weighed.   The increase in weight of each half cathode was taken as the weight of zinc deposited.

Chemical Attack on the Cathode.

It was recognised that any form of chemical attack on the cathode material by the plating solution would introduce an error which might conceivably be seriously large.   Tests were made by immersing in the bath pieces of the cathode material in the same condition as used for the actual throwing power experiments, and by suitable weighings determining the alteration of weight.   With the solutions and cathode material used in this work the alteration of weight was always small and never exceeded 1 mg. per half cathode for the normal period of test.   The weight of zinc deposited varied from approximately 4 gm. to 0·4 gm. on the two half cathodes in the zinc sulphate baths and from 0·9 gm. to 0·13 gm. in the cyanide bath.

With duralumin and aluminium cathodes a slight darkening on the sides remote from the anode was observed.   This proved to be due to a very slight deposition of zinc, but tests indicated that this would produce an even smaller error than possible chemical attack and if due to chemical replacement of the aluminium by zinc these two errors would tend to neutralise each other.

Correction for Uneven Temperature in the Bath.

No mention of the need for a correction due to uneven heating of the plating bath during a throwing power experiment was made by Haring and Blum.[1]   At first no attempt was made to correct any error due to this cause and it was found that, using a normal zinc sulphate solution, throwing power values determined were negative and were not generally reproducible.

After several experiments had been made it was found that the portions of the plating bath between each half cathode and the anode were heating unevenly and temperature differences as great as $5 \cdot 1°$ C. were recorded in an hour's run. In an ordinary plating bath similar conditions would not normally arise as convection currents in the liquid would keep the bath at very nearly the same temperature, or certainly the path through the electrolyte of the high current density would be very unlikely to become much warmer than the rest of the bath in the vicinity. It was therefore decided to look for a means of correcting for the unevenness of temperature.

A thermometer was placed midway between each half cathode and the anode with the bulb as nearly as possible at the centre of the cross section of the solution in the bath. Readings were taken at the beginning and at regular intervals during the period of the experiment. The mean value of the readings of each thermometer was taken as the mean temperature of the portion of the bath between the anode and the corresponding half cathode. It is recognised that this is only an approximation, but it is probably well justified. Haring and Blum showed that on each side of the anode, in a bath of this design, the current density was constant over the whole cross section of the bath. From this it is clear that the heating due to the electric current must be uniform on each side of the anode, as the bath was thoroughly stirred before each experiment. Movement of the bulb of the thermometer during an experiment did not reveal any large variation of temperature in different positions on the cross section. The value of the conductivity of the bath for each of the two mean temperatures was obtained by interpolation in the conductivity temperature curve. (See Appendix.) From this a corrected primary current ratio was calculated.

If t_1 and t_2 are the mean temperatures in the cell set for a primary current ratio of K : 1 and t_1 is greater that t_2, and C_1 and C_2 are the respective conductivities of the bath at t_1 and t_2. Then, since the cross section of the bath is the same on both sides of the anode, and the potential differences between both half cathodes and the anode are equal, therefore, ignoring polarisation, the current densities on each side of the anode are proportional to the conductivity and inversely proportional to the distance from the anode to each half cathode respectively. Thus the primary current ratio when corrected becomes : - -

$$C_1 \times K : C_2 \text{ or } \frac{C_1 K}{C_2}$$

and the corrected throwing power

$$\left(\frac{C_1 K \cdot C_2 - M}{C_1 K \cdot C_2} \right) 100 \text{ per cent.}$$

or if the corrected primary current ratio is written K corrected throwing power $= \frac{(K' - M)}{K'} 100$ per cent.

This correction has been found to alter the throwing power value very considerably, particularly with high primary current ratios, and in the case of the zinc sulphate plating baths.

At first, surprise was felt that the throwing powers determined by Haring and Blum by this method corresponded very closely with the throwing power calculated from potential measurements taken during their experiments. A small quantity of solution of the composition used by these workers ($1 \cdot 5$ N copper sulphate, $1 \cdot 5$ N sulphuric acid) was made up and its conductivity-temperature curve was determined. It was found to have a conductivity six times as great and a percentage increase in conductivity

per °C. only half that of the normal zinc sulphate bath used. A rough calculation, involving assumptions concerning the quantity of heat lost from the bath on each side of the anode, indicated that the correction required for Haring and Blum's solution was very small and would probably be within the limits of experimental error.

Effect of Current Efficiency on Throwing Power.

The cathode current efficiency-current density curves for two baths (*a* and *c*) were determined and are reported in detail in the appendix. In both cases the curve rose steeply to a maximum and then fell again less steeply as the current density increased from 1 amp. per sq. ft. The appreciable variation of cathode current efficiency with cathode current density has a marked effect on the throwing power. This can be readily appreciated from the formula deduced by Haring and Blum.[1]

Where T = throwing power.

e_f = cathode single potential on part of cathode far from the anode.

e_u = cathode single potential on part of cathode near the anode.

E_f = potential drop through solution only, from anode to far part of cathode.

$$T = 100\left(\frac{e_f - e_u}{E_f}\right)$$ only when the cathode current efficiencies on both parts of the cathode are the same. If the cathode current efficiencies on the two parts of the cathode differ and are designated by D_f and D_u respectively.

$$T = 100\left[1 - \frac{D_u}{D_f}\left(1 - \frac{e_f - e_u}{E_f}\right)\right].$$

Plating Solutions Used in these Experiments.

The throwing power under certain conditions has been determined of the following zinc plating solutions.

> (*a*) Normal zinc sulphate.
> 0·25 N sodium acetate.
> 1 gram/litre of gum arabic.

The zinc sulphate used was of "A.R." quality, the sodium acetate was "recrystallised." Both of these chemicals and the gum arabic were obtained from Messrs. British Drug Houses, Ltd. The acidity of the bath was adjusted by the addition of pure sulphuric acid to a p_H value of 4·0 and was kept at this value ± 0·1 by further suitable additions of sulphuric acid.

> (*b*) 2 N zinc sulphate.
> 2 N sodium chloride.
> 0·25 N sodium acetate.
> 1 gram/litre gum arabic.

This bath was not specially made up for the work in hand, and had been used for previous experiments. The chemicals were of the same quality as those used for (*a*) and the sodium chloride was of "recrystallised" quality. The p_H value was maintained at 4·0 as in solution (*a*).

> (*c*) Normal zinc cyanide.
> 0·75 normal sodium cyanide.
> 0·5 normal ammonium hydroxide.

The zinc and sodium cyanides were obtained as "pure" chemicals and when dissolved together gave a pale yellowish-brown coloured solution. The normality with respect to ammonium hydroxide can only be considered to be approximate.

The ammonium hydroxide tended to evaporate from this solution and small quantities had to be added from time to time to make up the loss, in consequence its concentration varied from the stated value. The cyanide content of the bath was also rather uncertain owing to its decomposition. When there was evidence of the bath requiring an addition of cyanide, ammonium cyanide was added in order to avoid increasing the sodium content of the bath. The ammonium cyanide was prepared by adding ammonium sulphate to barium cyanide solution and filtering off the precipitate. The solution was rendered ammoniacal in order to minimise the loss of hydrogen cyanide.

Throwing Power—Primary Current Ratio.

The throwing power of the three different baths was determined, in each case with primary current ratios varying from 2 : 1 to 9 : 1. Duralumin was used for the cathodes and was prepared as has been previously described. In Table I. the values obtained for plating baths (a), (b), and (c) respectively are recorded and are plotted in Fig. 1. The corrected primary current ratio and the corrected throwing power are also included. The temperature of the plating baths was maintained as nearly as possible at 20° C.

TABLE I.

Plating Conditions.	Primary Current Ratio.	Metal Ratio.	Throwing Power Per Cent.	Corrected Primary Current Ratio.	Corrected Throwing Power Per Cent.
Plating bath (a).	2 : 1	2·068 : 1	− 3·4	2·093 : 1	+ 1·19
p_H 4·0. Period	3 : 1	3·130 : 1	− 4·33	3·167 : 1	+ 1·17
of deposition 1	4 : 1	4·221 : 1	− 5·53	4·260 : 1	+ 0·92
hour. Mean	6 : 1	6·413 · 1	− 6·88	6·353 : 1	− 0·95
C.D.—18 amp.	9 : 1	9·736 : 1	− 8·18	9·393 : 1	− 3·65
per sq. ft.					
Plating bath (b).	2 : 1	1·994 : 1	0·30	2·057 : 1	3·06
p_H 4·0. Time	3 : 1	2·959 : 1	1·37	3·091 : 1	4·27
of deposition 1	4 : 1	4·034 : 1	− 0·85	4·097 : 1	1·54
hour. Mean	6 : 1	6·064 : 1	− 1·07	6·243 : 1	2·87
C.D.—18 amp.	9 : 1	8·941 : 1	0·66	9·260 : 1	3·45
per sq. ft.					
Plating bath (c).	2 : 1	1·750 : 1	12·5	2·004 : 1	12·5
Time of de-	3 : 1	2·580 : 1	14·0	3·021 : 1	14·6
position 1 hour.	4 : 1	3·332 : 1	16·7	4·040 : 1	17·6
Mean C.D. 4	6 : 1	4·800 : 1	20·0	6·061 : 1	20·8
amp. per sq. ft.	9 : 1	6·977 : 1	22·4	9·100 : 1	23·3

The value for a primary current ratio of 3 : 1 for bath (c) does not fall on the curve given by the other points. In an attempt to find a reason for this the throwing power with a ratio of 3 : 1 was later redetermined. This time a corrected throwing power of 17·44 per cent. was obtained, but since the composition of the bath alters from time to time it is probable that this value is not strictly comparable with those of previous determinations.
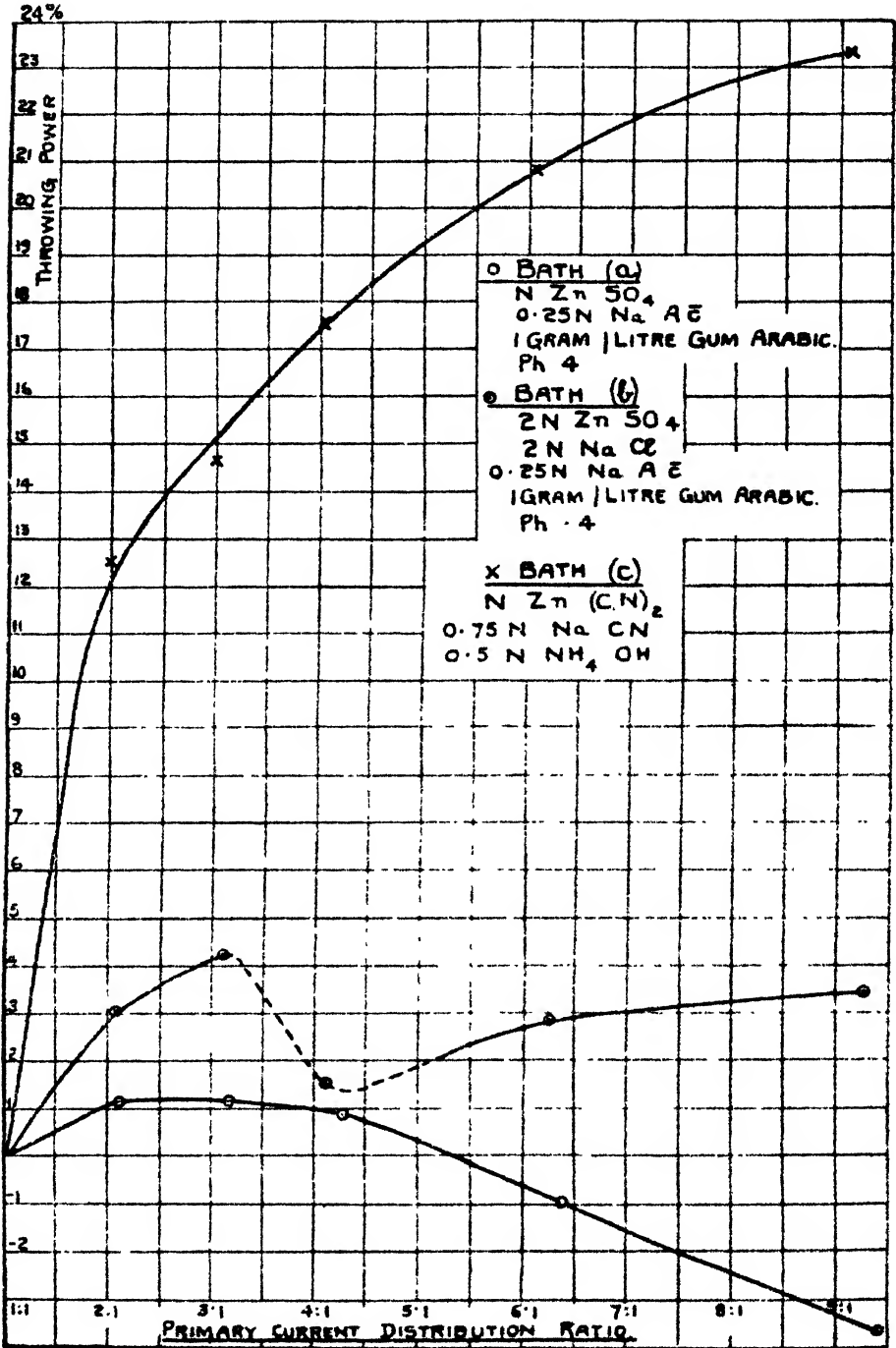
FIG. I.—Throwing power-primary current distribution ratio curves.

Effect of Cathode Material on Throwing Power.

Throwing power determinations were made, using cathodes of materials other than duralumin, in plating baths (a) and (c). A primary current ratio of 4 : 1 was used and current densities of 18 and 4 amp. per sq. ft. respectively with the two solutions. The values obtained are given in Table II., are corrected for temperature difference in the two parts of the throwing power cell and are each the mean of two determinations unless otherwise stated.

TABLE II.

Plating Conditions.	Cathode Material.	British Standard Specification.	Corrected Throwing Power.	
			Plating Bath (a).	Plating Bath (c).
Primary current ratio, 4 : 1	Duralumin	3L·3	+0·92 per cent.*	17·6 per cent.*
Mean C.D. :	Aluminium	2L·16	+3·25	23·0
(a) 18 amp. per sq. ft.	Zinc	—	−3·05	20·0
	Copper	2B·4	+2·20	16·2
(c) 4 amp. per sq. ft.	Brass	2B·12	+4·45	9·6
	Mild steel	2S·3	—	—
	(a) Sand blasted	—	−2·75	about − 1700
	(b) Pickled	—	—	+22·5*

Mild steel cathodes in the cyanide plating bath give a very good extreme example of the effect of varying the method of surface preparation. In this bath the hydrogen overvoltage of sandblasted mild steel appears to be low and during electrolysis there is a very vigorous evolution of hydrogen. Also the cathode current efficiency was much lower on the low current density portion of the cathode than on the high current density portion, resulting in a very low throwing power value. The throwing power on pickled steel was of the same order as that on Aluminium.

Comments and Conclusions.

Numerous methods have been published for determining throwing powers of plating baths. The only one of which the author has heard, that attempts with reasonable success to correlate the better known propertiesof a plating bath with its throwing power, is that due to Haring and Blum.[1]

Haring and Blum demonstrated the connection between the weights of metal deposited on two different parts of a cathode, the resistances through the plating bath from the anode to the two parts of the cathode, the slope of the electrode potential-current density curve and the shape of the cathode current efficiency-current density curve. Thus the values obtained by this method have a definite mathematical significance and are not purely arbitrary as with most other methods.

With most plating baths it has now been found necessary to make a correction for the change of conductivity of the bath with change of temperature, caused by uneven heating, due to different current densities in different parts of the Haring and Blum apparatus. With baths of high conductivity or those used with low current densities this correction may be negligibly small.

* These values are from single determinations.

Following are points which, in addition to the above, should be observed when using the apparatus :—

1. A series of determinations with different primary current ratios should be made for each bath tested. Ratios varying from 2 : 1 to 9 : 1 are obtainable with the apparatus used.

2. The shortest distance between the anode and a half-cathode must be kept constant. With the apparatus as at present designed a distance of 5 cm. is suggested as being suitable.

3. The mean current density should be kept constant throughout each series of tests.

4. The temperature of the plating bath should be kept as nearly as possible constant.

5. The anode should preferably be made of wire gauze, but failing this, sheet material with numerous holes drilled through it should be used.

The throwing power of the normal zinc sulphate solution (bath (a)) was found to increase with primary current ratio to slightly over + 1 per cent. with a primary current ratio of 2 : 1, after which it decreased gradually to − 3 per cent. with a primary current ratio of 9 : 1.

The throwing power of (bath (b)) the twice normal zinc sulphate solution was slightly better. It rose to a maximum of + 4 per cent. with a primary current ratio of 3 : 1, fell to a minimum of + 1 per cent. at 4 : 1, and rose gradually to + 3 per cent. at 9 : 1. This last rise in the curve is considered to have been influenced by the somewhat "treed" deposit which formed on the high current density half cathode. It is possible that some of the trees became detached before the half cathode was weighed.

Bath (c)—the normal zinc cyanide solution—gave a throwing power of 12 per cent. with a primary current ratio of 2 : 1, and the value increased steadily to 23 per cent. with a primary current ratio of 9 : 1. This bath has a satisfactory throwing power. The two sulphate baths have not, and can only be relied on to give metal ratios approximately equal to the primary current ratios.

Different cathode materials were found to give different throwing power values and the method of preparation of mild steel cathodes was found to influence the throwing power to a remarkable extent. It is suggested that the sandblasting may roughen some materials more than others and that this may alter the cathode current efficiencies and the effect of polarisation.

APPENDIX.

Determinations of Conductivity of the Plating Solutions Used.

The apparatus used for the determination of conductivity consisted of a Wheatstone bridge arrangement using a 10 metre bridge wire arranged helically on a drum, a suitable fixed resistance and a buzzer transformer device for supplying suitable alternating current. A pair of telephones were used for finding the point on the bridge wire which gave a balance. No amplifying device was used. The conductivity cell was of a common design and had two circular platinum electrodes each 10 mm. in diameter arranged vertically one above the other. The electrodes were coated with platinum black.

The conductivity cell was placed on a stand in a 300 c.c. beaker which also contained a hand stirrer and a thermometer was supported by an asbestos disc

which served as a lid. The beaker contained water and was surrounded by a lagging of heat insulating material. Before any readings were taken, the temperature was allo wed to come to a steady value. It was recognised that this was not so satisfactory as a thermostatically controlled enclosure, but for this work it was considered to be sufficiently accurate. When the cell was approximately 20° C. and the room temperature 31° C. a rise in temperature 1° C. in the cell was observed in 1½ hours. The cell was calibrated with normal potassium chloride solution.

The conductivity values are recorded in Table III. and are plotted in Fig. 2.

TABLE III.

Plating Bath.	Temperature, °C.	Conductivity mhos per cm. cube.	Specific Resistance, ohms per cm. cube.	Remarks.
N zinc sulphate	16·5	0·0338	29·59	The temperature
0·25N sodium acetate	18·0	0·0351	28·51	coefficient is
1 gram per litre gum	18·8	0·0359	27·86	0·000826 mhos
arabic	19·6	0·0363	27·55	per cm. cube per
p_H 4·0	21·3	0·0375	26·67	°C. or 2·25 per
	22·4	0·0387	25·84	cent. per °C. at
	24·0	0·0399	25·06	25° C.
	25·4	0·0411	24·33	
	26·8	0·0426	23·47	
	26·6	0·0438	22·83	
	32·6	0·0474	21·10	
	35·9	0·0502	19·92	
1·5N copper sulphate	21·	0·229	4·367	The temperature
1·5N sulphuric acid	23·5	0·235	4·255	coefficient is
(Haring and Blum	26·5	0·243	4·115	0·00251 mhos per
solution)	32·3	0·256	3·906	cm. cube per °C.
				or 1·11 per cent.
				per °C. at 25° C.
2N zinc sulphate	18·5	0·0889	11·24	The temperature
2N sodium chloride	20·4	0·0927	10·79	coefficient is
0·25N sodium acetate	22·3	0·0966	10·35	0·00215 mhos per
1 gram per litre gum	23·7	0·0996	10·04	cm. cube per °C.
arabic	24·6	0·1021	9·79	or 2 09 per cent.
p_H 4·0	25·9	0·1047	9·55	per °C. at 25° C.
	28·9	0·1110	9·01	
	31·2	0·1162	8·60	
N zinc cyanide	20·0	0·0411	24·32	The temperature
0·75N sodium cyanide	21·6	0·0424	23·60	coefficient is
0·5N ammonium	24·7	0·0452	22·13	0·00101 mhos per
hydroxide	27·0	0·0478	20·91	cm. cube p r °C.
	30·3	0·0511	19·55	or 2·19 per cent.
	34·1	0·0553	18·09	per °C. at 25° C.
	36·5	0·0579	17·27	

Cathode Current Efficiency.

The cathode current efficiencies of solutions (*a*) and (*c*) with various current densities were determined. The throwing power cell was used and the cathode plate, 10 cm. × 10 cm. exposed in the solution to plating, was in each experiment made of duralumin. The bath was not stirred and the temperature was maintained as nearly as possible at 20° C. Conditions generally were maintained the same as during a throwing power determination. Currents up to 1 amp.
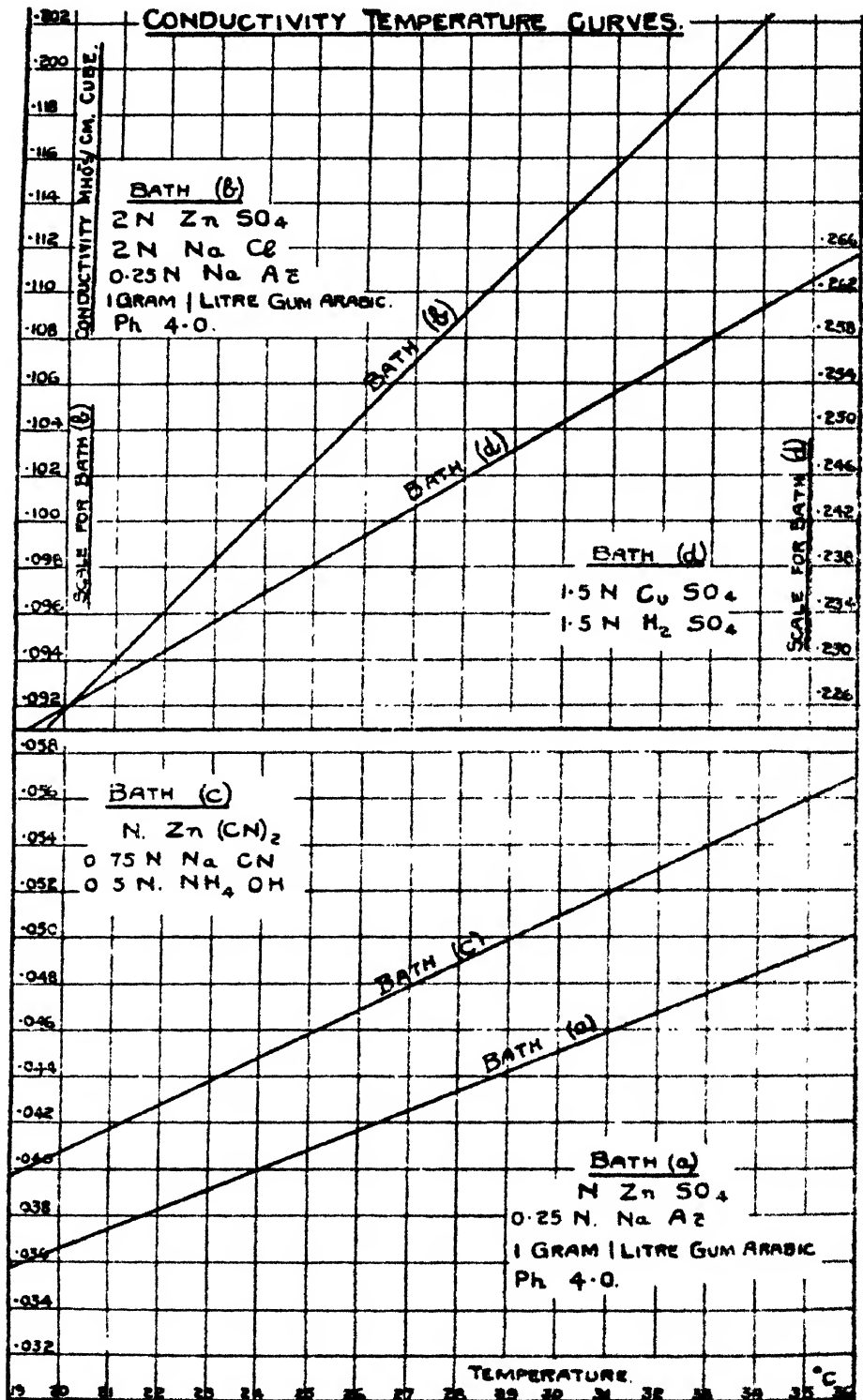
FIG. 2.

were measured by a Weston milliammeter with a 5-inch scale and above that were measured on an ammeter with scale readings occupying 1 inch per amp.

The quantity of electricity was measured by copper coulometers in which the electrolyte was stirred. A small quantity of ethyl alcohol was added to the electrolyte to prevent oxidation of the cuprous ions and the current density was kept between 2·1 and 21 amps. per sq. ft. Under these conditions the coulometer appeared to work satisfactorily.

The values obtained are recorded in Table IV. and are plotted in Fig. 3.

TABLE IV.

Plating Bath.	Current Density, amps. per sq. ft.	Cathode Current Efficiency, Per Cent.	Notes on Deposits.
N zinc sulphate 0·25N sodium acetate 1 gram per litre gum arabic p_H 4·0	1	94·66	Very dark grey.
	2	94·75	Dark grey.
	4	96·65	Light grey—smooth.
	6	98·11	Light grey—smooth.
	10	99·80	Light grey—smooth.
	20	99·04	Light grey, gas pits, and slight treeing.
	30	98·93	Light grey, vertical streaks, gas pits, and slight treeing.
N zinc cyanide 0·75N sodium cyanide 0·5N ammonium hydroxide	1	92·32	Rather dark, slight vertical streaks.
	2	96·45	Lighter, smooth, slight vertical streaks.
	3	98·22	As with 2 amps. only streaks more marked.
	4	97·63	Light, smooth, slight streaks, best deposit.
	6	97·07	Darker slight streaks.
	8	96·56	As 6 amps. per sq. ft. only black speckles.
	12·4	96·29	Dark, speckled, and rough.
	15	95·10	Dark and marked trees.
	20	92·21	Very dark and badly treed.

During the course of the work it was suspected that for a short period after the cathode was placed in the solution the cathode current efficiency was lower than that represented when a period of 1 hour was allowed for deposition. This was tested by determining the cathode current efficiency with shorter periods of deposition. The values obtained are given in Table V.

TABLE V.

Plating Bath.	Current Density, amps. per sq. ft.	Period of Deposition, Mins.	Cathode Current Efficiency, Per Cent.
N zinc sulphate 0·25N sodium acetate 1 gram per litre gum arabic p_H 4·0	18	2·5	98·19
	18	15	99·54
	18	60	99·20*
	4	2·5	97·66
	4	60	96·65
N zinc cyanide 0·75N sodium cyanide 0·5N ammonium hydroxide	6	2·5	96·42
	6	5	94·52
	6	60	94·66

* Interpolated from curve, Fig. 3.

These results do not indicate a decreased cathode current efficiency with short periods of deposition.   The very short period determinations have a much
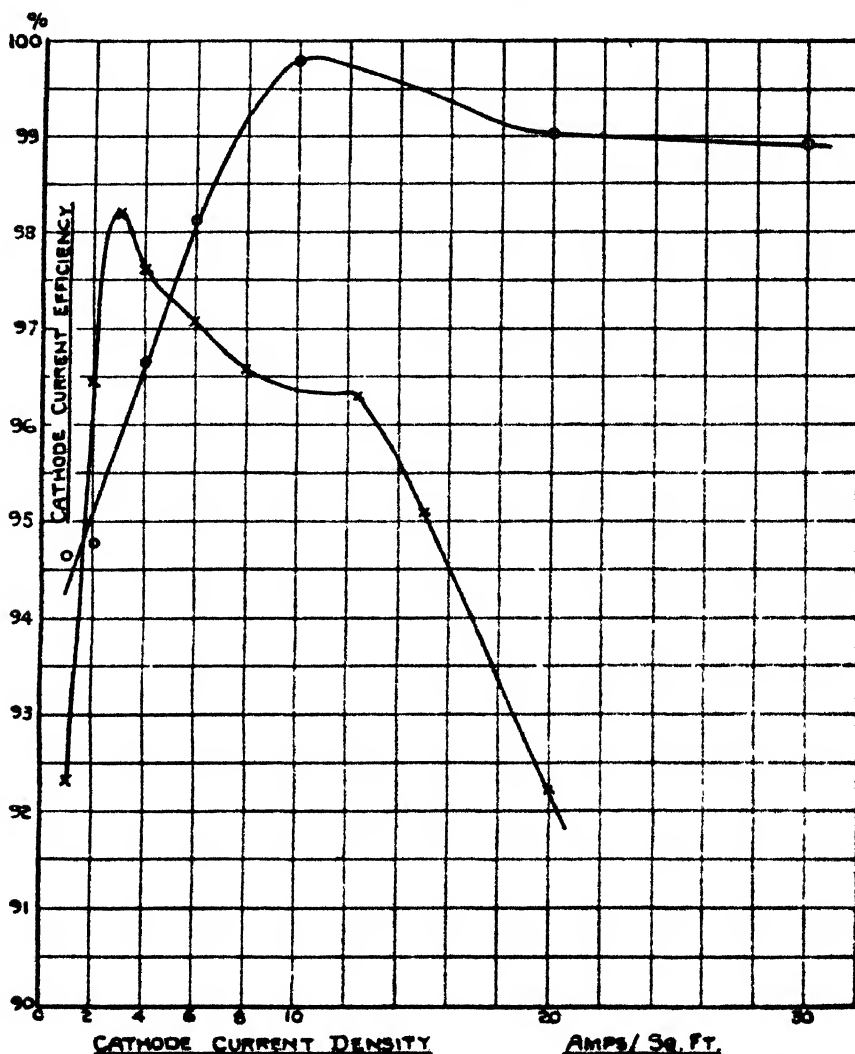
Fig. 3.--Cathode current efficiency—cathode current density curves.

⊙ Bath (a)
   N. Zn SO₄
   0·25N. Na A⁻_c
   1 gram/litre gum arabic
   P_H 4·0

× Bath (c)
   N. Zn (CN)₂
   0·75N. Na CN
   0·5N. NH₄OH

lower degree of accuracy than those of 60 minutes duration, owing to the very small weights of metal deposited, and this probably accounts for the variation of current efficiency observed.

DIFFRACTION OF ELECTRONS BY THIN FILMS OF NICKEL AND COPPER OXIDE.

By James A. Darbyshire.

When a strip of metal is heated in a flame, a thin layer of oxide is formed on the surface, generally showing characteristic interference tints varying with the thickness of the layer.

U. R. Evans [1] has indicated a method by which these oxide films can be removed by a process of electrolytic corrosion.

The electrodes are cut from sheets of copper and nickel foil 0·015 cm. in thickness and are approximately 3·5 by 1·5 cm. in area. These pieces of foil are cleaned with fine emery paper (ooo), and then one of them is heat-tinted by inserting the edge into the flame of a Bunsen burner until the required tint is attained. The electrodes are then fixed in position in the electrolytic cell, which is a simple U-tube, the lower bend being filled with a number of glass beads to assist in the formation of the diaphragm of membraneous hydroxide. The electrolyte consists of saturated potassium chloride for nickel, and saturated potassium sulphate for copper ; this was poured into the electrolytic cell until about 3 cm.^{2} of the electrodes were covered.

The heat-treated electrode is made anode and the cathode consists of a similar strip of the same metal which has not been oxidised. A current of 50 milliampères is then passed through the cell for about five minutes, when the oxide skin on the anode will be seen to be hanging loose. If it is merely blistering in places the process is continued until the skin appears to be quite loose.

After loosening, the films are washed off the metal into a bath of warm water, and are then caught on to a small brass washer having a hole (1 mm. diameter) in the centre. After a little practice it is possible to catch the film so that it covers the hole quite uniformly. This washer is then attached to the holder in the electron diffraction apparatus by means of " clear belco " nitrocellulose varnish.

The nickel oxide films were transparent and almost colourless by transmitted light, and very pale pink by reflected light.

The copper oxide films were transparent, and very faintly orange by transmitted light, but if prepared by heating the copper to redness they were much more strongly orange and apparently too thick for successful work with electrons. The electron beams were recorded photographically after transmission directly through the thin films, the films being apparently thin enough to render this method quite effective.

The measurements made on the photographic plates are given in Table I. The voltage applied to the electron tube was measured by means of a spark gap ; it was found advisable, however, to take photographs of one specimen over a whole range of voltages from 10 to 40 kV and then plot a curve of the radius of one definite and accurately measurable ring against the voltage. Occasionally a surge would cause a large

[1] *J. Chem. Soc.*, 2651, 1929.

error in the voltage measurement by spark gap method, and the above procedure would indicate any such irregularity.

A screen was inserted into the circular aperture of the camera, thus allowing only a diametral strip of any ring pattern to be recorded on the plate. In this way six or even more exposures can be made on one plate at different voltages, the plate being lowered a finite amount between each exposure.

One exposure, from which calculations were made, was then taken without the screen, thus recording the complete ring system on the plate (Fig. 1). The voltage for this exposure was measured directly, and also read off from the curve mentioned above, thus confirming the direct measurements.

TABLE I.

Plate I.—Nickel Oxide. Voltage, 41,500.

Ring.	Radius (cm.).	Intensity Estimated.	d/n Obs.	Plane.	a_0.
1	0·61	18	2·39	111	4·13
2	·71	20	2·04	200	4·09
3	1·00	12	1·45	220	4·11
4	1·19	4	1·22	311	4·06
5	1·23	4	1·18	222	4·09
6	1·45	2	1·00	400	4·01
7	1·56	5	0·93	{ 331 / 420 }	4·11
8	1·73	4	·84	42'	4·12
9	1·84	2	·79	511	4·10
10	2·00	1	·72	440	4·07
11	2·10	1	·69	{ 531 / 600 }	4·11
12	2·15	1	·67	620	4·20
				Mean . .	4·10 Å

a_0 = side of elementary cube in Å.

The d, n values are calculated from the observed radii of the rings by means of the formula,

$$d\,n = \frac{12 \cdot 25 \times L}{r\sqrt{P}(1 + 4 \cdot 92 \times 10^{-7}\,P)}.$$

The coefficient of P in the bracket in the denominator is due to the relativity correction for variation of electron mass with velocity, and this term can be neglected for voltages below 50 kV.

In the above formula n is the order of the interference, and L is the distance from the specimen to the photographic plate. P is the accelerating potential in volts.

If we compare these figures d/N for the planar spacings, with those given by G. R. Levi and G. Tacchini,[2] we see that they agree closely with their values for nickel monoxide. The glancing angles of reflection given in their paper are converted into d/N values and are given for comparison in Table II.

The intensities of the diffraction spectra can be calculated theoretically on the basis of wave mechanics, making use of Mott's' formula for the elastic scattering of electrons by atoms.

[2] *Gazz. Chim. Ital.*, **55**, 28.

N_2O
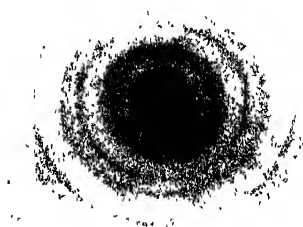
Ca_2O

Fig. 1.

The intensities for the small angles used here are given by the formula,

$$I = \frac{kS^2p}{\theta^2},$$

where S is the structure factor, calculated just as in the case of X-ray diffraction, except for the fact that "f" values are read off from the electron "f" curve (not the X-ray "f" curve), the relationship between the two curves being

$$f' = \frac{8\pi^2 mc^2}{h^2}\left(\frac{z - f}{\left(\frac{4\pi}{\lambda}\sin\frac{\theta}{2}\right)^2}\right),$$

z is the atomic number of the scattering atom, θ the angular deflection of the diffracted beam, p is the number of co-operating planes.

TABLE II.

d/n Electron Diffraction.	Intensity Estimated.	d/n NiO.	I Calculated Electron Diffraction.
2·39	18	2·33	7·7
2·04	20	2·03	13·3
1·45	12	1·45	6·5
1·22	4	1·23	1·1
1·18	4	1·19	1·6
1·00	2	1·03	0·5
0·93	5	{ 0·95 / ·93	0·3 } / 1·5 }
·84	4	·85	0·9
·79	2	·80	·2
·72	1	--	·2
·69	1	—	·2
·67	1	—	·3

Calculation from Levi's figures gives $a = 4\cdot11$ Å. as compared with the value $4\cdot10$ Å. obtained above; both these are lower than the value $4\cdot175$ Å. obtained by Brentano[a] using precision measurements.

TABLE III.

Plate 2. Voltage, 35,000.

Ring.	Radius (cm.).	Intensity Estimated	d/n (Obs.).	Plane.	a_0 (in Å.)	d/n Cu₂O.	I Calc. for Cu₂O Electron Diffraction.
1	0·52	6	3·03	110	4·28	3·00	7·1
2	·63	20	2·50	111	4·31	2·45	80·8
3	·74	14	2·13	200	4·26	2·12	21·0
4	·90	2	1·75	211	4·28	1·73	1·7
5	1·03	12	1·53	220	4·32	1·50	20·3
6	1·22	12	1·29	{ 311 / 222 }	4·28	{ 1·28 / 1·22 }	13·5 } / 2·9 }
7	1·60	10	0·98	{ 331 / 240 }	4·31	{ 0·97 / ·95 }	3·7 } / 2·5 }
8	1·79	4	·88	422	4·30	·87	2·9
9	1·91	4	·82	511	4·26	·82	1·5
				Mean .	4·29 Å.		

Thus the oxide films formed on heat-tinted nickel are sufficiently crystalline to give good electron diffraction photographs, and the oxide is the usual face-centred form of nickel monoxide.

Measurements taken from the film removed from the copper strip are as Table III.

The values obtained by Niggli [4] for Cu_2O are given in the above table together with the intensities calculated as in the case of NiO for electron diffraction from the cuprite structure.

The agreement is quite good, both as regards d/n values, and intensities, with the exception of the 111 reflection, which does not appear to be as strong as the calculated value would indicate. This is most probably due to the limited range of the photographic plate, and is an effect which makes the accurate determination of intensities by photographic methods a rather complicated problem.

Niggli's work leads to a value 4·26 Å. for a_0 as compared with 4·29 Å. obtained above.

Thus there is quite good evidence for the nature of the crystalline structure of these thin oxide films. The former is the usual face centred NiO structure, the latter the usual cubic form of copper oxide, cuprite Cu_2O. No evidence of either metallic nickel or copper could be found; hence the metal, if present, is in too small proportions to be detected, or else it is present in some highly dispersed colloidal form.

[4] *Z. Kristall.*, **57**, 253, 1922.

REVIEWS OF BOOKS.

A Text-book of Thermodynamics. By F. E. HOARE, M.Sc., A.R.C.S., D.I.C. (London, Edward Arnold & Co, 1931. Pp. xii + 271. 21 × 13 cms. Figs. 49. Price 15s. net.)

The importance of thermodynamics in the physico-chemical world is sufficient justification for a new text-book on the subject. Much is to be gained by looking at a subject from different points of view. Mr. Hoare's aim has been to show the variety of subjects to which thermodynamics can be applied. The further aim of comparing theoretical deductions with experimental results has been kept in view throughout in order that those primarily interested in experimental work may appreciate more fully the aid rendered to them by mathematical physicists. This side of the subject might, however, have been considerably extended with advantage.

This volume is a serious contribution to the subject by one who has been brought up in the school of the late Professor Callendar. If at times he appears to stress the merits of the work that Callendar has done in devising simplified equations to represent the properties of steam at moderate densities, without at the same time indicating clearly the limitations of this work, he may perhaps be pardoned. It is a matter of surprise, however, that he has not availed himself of the opportunity of presenting a critical (or, at least, an expository) account of Callendar's more recent extensions of his work which are not even mentioned, important though they are.

In a general treatise on thermodynamics it is natural to expect more emphasis to be laid on attempts that have been made to represent the properties of fluids

over *wide* ranges of conditions, but the author scarcely gets beyond van der Waals' equation in this connection.

Besides the more classical portions, chapters are given on " The Equilibrium of Systems," " Gaseous Systems and the Nernst Heat Theorem," " The Thermo-dynamics of Dilute Solutions," " Applications to Electrical Phenomena," " The Thermodynamics of Radiation," and the work of Einstein, Nernst, Lindemann, and Debye concerning the specific heats of bodies at low temperatures.

The author has a good grip of his subject and in general knows how to present it. Occasionally there are imperfections. Thus (p. 55) in defining "total heat " the statement is made that " the term pv is the work done in ex-panding the substance from zero volume to the volume v against the pressure p." On p. 58, the term " reversible " is often used, but it requires to be used uniformly otherwise a student will be apt to think that in the cases in which it is omitted its presence is not required : there is no general heading indicating that reversibility is being generally assumed. In discussing the variations of specific heats it is rather a pity to employ Maxwell's thermodynamic relations so much ; the complete proofs are much shorter without reference to these and the logic is less involved. The exposition of le Chatelier's principle (p. 159) might be amplified by reference to the critical remarks of the late Lord Rayleigh.[1]

Since Callendar's equation is based upon the porous plug experiment, it is natural that this experiment and its interpretation should occupy a prominent place. Hoare's account is very much superior to that of the ordinary text-book ; but it could be much shortened and improved by departing from the historic practice of discussing the bearing on Mayer's and Boyle's laws. These two laws are not independent of one another and absence of cooling does not require that they be separately satisfied. There is so much new matter now known that it is necessary to discard much concerned with the early attempts to unravel a subject, especially when these have not proved particularly useful ; otherwise the subject becomes overburdened.

This section of the volume is strangely free from the experimental data on which Callendar's equation rests. The author no doubt realised that these had been fully given in Callendar's own work on the properties of steam ; nevertheless, it would have been in accordance with the author's professed aim to have given a short summary.

We have selected for comment from those parts of the book which exhibit the greatest novelty of treatment. With regard to the rest the reader will find the exposition usually lucid, though there is a tendency for the mathematical proofs to be unnecessarily long. The book is certain to meet with appreciation by students and other workers. It is probably not suitable for most beginners.

The Dipole Moment and Chemical Structure. Edited by P. Debye. Authorised translation by Winifred M. Deans. Pp. x + 134. (London and Glasgow : Blackie & Son, Ltd., 1931.) 10s.

This volume contains a series of lectures given at Leipzig in 1929 on a subject which owes its theoretical development very largely to Debye. The monograph by Debye on Polar Molecules forms, in fact, the best theoretical introduction to the subject matter of the present volume.

The measurements of dipole moments, which lay bare many of the details of molecular structure provide a powerful weapon for the study of the problems of

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[1] *Trans. Chem. Soc.*, CXI., 250 (1917).

valency and reactivity met with in organic chemistry. These problems are discussed by Estermann, Errera, Ebert, Hückel, and Wolf. Their lectures introduce no radical amendments into the theory of organic chemistry, but rather amplify and extend the views held by organic chemists on such subjects as the valency angle in carbon compounds, the possibility of free rotation about valencies and the influence of substitution on reactivity. The views of the organic chemists with regard to structure, hitherto amorphous, are rapidly becoming crystallised as a result of more definite proofs. Particular points of interest brought out in these lectures are the increase in the valency angle in dichloromethane due to the interaction between the chlorine atoms (Debye), the bending of oxygen and nitrogen valencies, the lack of rotation in certain molecules of the type C . a_4, the definite evidence yielded with regard to the structure of cis-trans compounds, and the support given to the theory of alternating polarity of aromatic derivatives.

Advances in the experimental methods are described by Sanger, Estermann, and Wolf. Sanger gives an account of an improved method of measuring the dielectric constants of gases at constant pressures, and Estermann has applied the molecular beam method to the study of the derivatives of penta-erithritol, the moments of which cannot be found by the dielectric constant method on account of their insolubility and low vapour pressures. The important fact is brought out that some of these derivatives do not possess tetrahedral symmetry. Wolf discusses the theory of the Kerr effect and shows how determinations of the "B" constant can be employed to amplify information gained from electric moments. It is possible by this method to deduce approximately the angle between the directions of the dipole moment and the maximum polarisibility, and hence to be able to make more definite statements with regard to valency angle.

The more general theory of the dielectric properties of molecules is examined by Ebert, who takes into account the effect of atomic mobility in the molecular framework. Of special interest to chemists is the discussion of the free rotation of the C—C and the C⁼C linkage with special reference to C_2H_6 and C_2H_4. Hund outlines the general methods of attack on the problem of structure by modern quantum theory.

There are also lectures on the liquid and solid state of matter. Errera discusses the polar and non-polar association which occurs in binary mixtures and their effects on the vapour pressure and viscosity of the solutions, and Errera and Hogendahl from somewhat different points of view examine the question of the mobility of atoms in crystals under the influence of electrical fields.

These papers bring out clearly the nature of the advances made in the study of dipole moments in recent years, and the importance of this method for the study of structural problems. They also underline the gaps in our knowledge and thus show the way to future work. Thus the volume will prove very valuable not only to workers in the field but also to those who are interested in the developments of organic chemistry.

W. E. G.

ERRATUM.

P. 601, line 7, for 128·78 read 123·78.

THE OXIDATION OF FUEL VAPOURS IN AIR.

By E. W. J. MARDLES.*

Abstract.

The investigation on the oxidation characteristics of fuel vapours in air has included experiments with different classes of hydrocarbons, alcohols, aldehydes, ether and with hydrogen, carbon disulphide, carbon monoxide, etc., and has been carried out with a view to determining the cause of the differences in behaviour of different fuels in the petrol engine.

A critical examination of the various hypotheses proposed for the mechanism of the first changes during combustion has been made; the peroxide theory of combustion propounded by Bach; Engler and Wild (1897); Grün; Kelber; Wartenberg and Sied (1920); and developed later by Callendar and Mardles; Moureu and Dufraisse (1927); Brunner and Rideal (1928); Stephens and others, appears to be the most promising and is supported in a great measure by recent experimental results. The theory affords a rational explanation of many phenomena recorded in the literature of combustion; thus, not only are autoxidation, autocatalysis and engine detonation accounted for by the action of peroxides, but the remarkable action of inhibitors or "anti-oxygens" and the mechanism of the formation of alcohols, aldehydes and other intermediate products of combustion can be explained in a simple and logical manner.

A study of the kinetics of oxidation of the fuel vapours in air shows that those fuel vapours which react relatively slowly and have a low temperature coefficient usually possess anti-knock properties, whilst heptane, ether and other pro-knock substances have a high temperature coefficient of gaseous reaction. Inhibitors invariably reduced the amount of peroxidation and so lowered the temperature coefficient of oxidation.

I. THE OXIDATION IN AIR OF (*a*) CARBON DISULPHIDE, AND (*b*) CARBON MONOXIDE.

The oxidation of carbon disulphide vapour in air is distinct in many ways from the slow combustion of hydrocarbon vapours although the general mechanism of oxidation appears to be the same in as far as the reactions are auto catalytic.

According to the Engler-Bach peroxide theory of combustion recently developed by Callendar and Mardles,[1] Moureu and others,[2] Egerton,[3] Brunner and Rideal,[4] etc., the catalyst is the activated complex of a fuel molecule and an oxygen molecule, the so-called peroxide or moloxide, which is capable of initiating chains of reactions including autoxidation.

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* Air Ministry Laboratory, Imperial College of Science, S.W. 7.
[1] *Engineering*, 4th February, 1927.   [2] *Ann. Off. Nat. Comb. Liq.*, 2, 233, 1927.
[3] *Nature*, 120, 694, 1927.   [4] *J.C.S.*, 1162, 1928.

The moloxide by reaction with another molecule of fuel or of a substance such as toluene which can act as an inhibitor, loses a part or the whole of its energy and ceases to be a catalyst.

According to Bach [5] carbon monoxide first forms the complex $CO(O_2)$ which accelerates the oxidation. Bach carried out a series of experiments to demonstrate the possibility of the formation of this compound, percarbonic anhydride,

$$CO + O_2 \longrightarrow O = C{\displaystyle \diagup^{O}_{\diagdown O}}$$
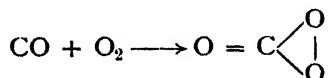
which he considered caused the reactions that Traube attributed to hydrogen peroxide. The combustion of carbon monoxide can be inhibited and influenced by numerous substances, so indicating the primary formation of a catalyst. Egerton has found that during the combustion of carbon monoxide in air the presence of approximately one thousandth part of iron carbonyl reduces the rate of flame to a quarter of its normal rate. Both carbon disulphide and carbon monoxide are sensitive to inhibitors during oxidation, and it will be shown later that though the oxidation of carbon monoxide and carbon disulphide can be inhibited, they in their turn behave as inhibitors during the combustion of hydrocarbons and increase anti-knock action.

Mixture strength per cent. weight fuel in air.

FIG. I., 1.—The effect of mixture strength on temperature of initial oxidation of (a) carbon monoxide, (b) iso pentane, (c) carbon disulphide (self-ignition), (d) carbon disulphide (chemi-luminescence); tube method.

An interesting feature of the combustion of carbon disulphide is that with increase in the richness of the mixture there is a considerable decrease in the tendency to oxidise and to self-ignite.

Carbon monoxide has a different behaviour in this respect and resembles the hydrocarbon vapours; the richer mixtures tend to oxidise at lower temperatures. This is shown in Fig. 1.

The study of the oxidation characteristics of different hydrocarbons has shown that those fuels which are prone to oxidise readily and to possess low self-ignition temperatures or to exhibit chemiluminescence usually induce knocking in the internal combustion engine,[6] but carbon disulphide, although easily oxidised at relatively low temperatures with considerable chemiluminescence, yet possesses an anti-knock action. The addition of carbon disulphide to petrol in the proportion, 80 volumes petrol: 20 volumes carbon disulphide, was found to raise the Highest Useful Compression Ratio (H.U.C.R.) from 4·75 to 5·25.[7]

[5] *Moniteur Scientifique*, **11**, 479, 1897.
[6] *Cf.* Moureu and co-workers, *loc. cit.*,[2] Berl, Heise and Winnacker, *Z. physic. Chem.*, **139**, 453, 1928.
[7] *Cf.* also Ricardo, *Inst. Aut. Eng.*, Report of the Empire Fuel Committee, **18**, 144, 1924.

The anti-knock action of carbon disulphide and of carbon monoxide is indicated by the relatively low temperature coefficient of gaseous reaction.

Tizard and Pye [8] concluded from their researches on the adiabatic compression of various fuel vapours in air that the anti-knock properties are associated with a low temperature coefficient of reaction, the pro-knock hydrocarbon heptane and ethyl ether possessing considerably higher coefficients than carbon disulphide.

The action of anti-knocks and inhibitors is invariably that of reducing the temperature coefficient of gaseous reaction, and this behaviour may be explained on the peroxide theory of detonation by assuming that at all temperatures the inhibitors control the rate of accumulation of active peroxides. In this way the rate of oxidation is considerably reduced and the temperature of self-ignition raised, it being considered that the rate of reaction is a function of the concentration of active peroxides.

(a) The Oxidation in Air of Carbon Disulphide Vapour.

The oxidation of carbon disulphide vapour in air occurs to a small but measurable extent below 100° C. ; Berthelot [9] has shown that at ordinary temperatures and pressures in diffused light no appreciable change took place during the period of a year. A very faint fog, visible in a Tyndall cone, begins to form when carbon disulphide vapour is heated in air just below 100° and the change is usually accompanied by a slight fall in pressure.[10] Measurements of the pressure changes accompanying oxidation of a gas mixture can be conveniently carried out by means of an

(a) At 160°, different mixture strengths. Mixture strengths of curves reading from left to right: 4·5 per cent., 6·2, 10·0, 16·0 and 35·5. (Self-ignition occurred in the first two cases after a few minutes' heating.)

(b) At different temperatures, 37 per cent. mixture strength. Temperatures of curves reading from left to right: 250°, 210°, 170°, 150° and 100° C.
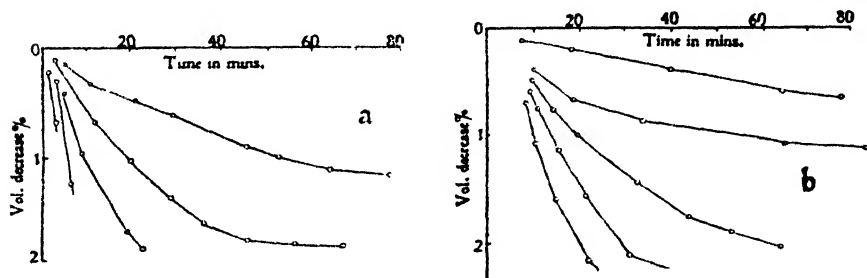
FIG. 1., 2.—Volume changes during the heating of carbon disulphide vapour in air.

apparatus already described,[11] in which the gas mixture is heated in a glass bulb and the pressure due to chemical change is observed from time to time by means of a toluene gauge, the pressure due to temperature difference being compensated for by means of another bulb such as in Callendar's compensated air thermometer.

By this method, it has been found that at ordinary room temperatures a 6·2 per cent. weight carbon disulphide air mixture remained without any change in volume greater than 0·1 per cent. over a period of two months

[8] *Phil. Mag.*, **79**, 1922.　　　　　[9] *Comptes rendus*, **126**, 1060, 1898.
[10] Gill, Mardles, and Tett, *Trans. Far. Soc.*, **24**, 574, 1928.　　[11] *J.C.S.*, 872, 1928.

whilst the same mixture at 35°-40° C. showed a decrease in volume of about 0·2 per cent. after a week. At 50°, the volume change was still small and at 75° amounted to about 0·5 per cent. after three hours when little further change occurred. Experiments were carried out at 100° with different strength mixtures and these showed volume decreases up to about 1 per cent. within four or five hours, the changes being more rapid and larger with the weaker mixtures.

With rise of temperature above 100° the weaker mixtures were liable to self-ignite; results obtained at 160° with different strength mixtures are shown in Fig. 2a; differences observed by varying the temperature from 100° to 250° for a 37 per cent. mixture are shown in Fig. 2b.

Temperature Coefficient of Oxidation in Relation to Detonation in an Engine.—It will be observed that an increase in mixture strength results in less oxidation as measured by volume decreases whilst with rise in temperature for a 37 per cent. mixture surprisingly small increases in the rate of oxidation were found. The low temperature coefficient of oxidation can be shown in another way described next.
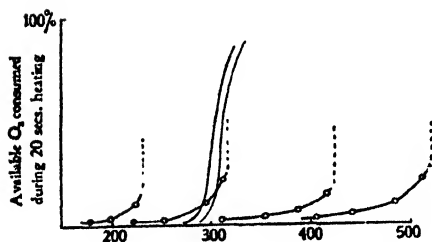
FIG. I., 3.—The oxidation of carbon disulphide—air mixtures of different mixture strengths—compared with that of normal hexane and ether. Mixture strength for curves, reading left to right: 9·5 per cent., 15 per cent., 22 per cent., and 39 per cent. The dotted portion of the curve represents the stage of self-ignition. The complete curves are for ethyl ether (left) and normal heptane (right).
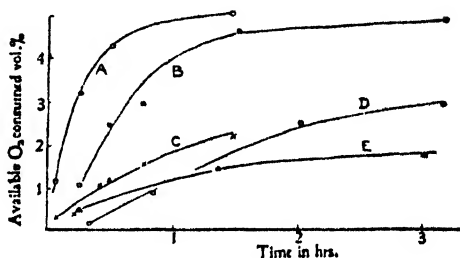
FIG. I., 4.—The oxidation of carbon disulphide in air—rate of depletion of oxygen with time. A. 35 per cent. CS₂ at 230° C.; B. ditto at 180° C.; C. ditto at 180° C. with the addition of approximately 10 per cent. nitrogen peroxide; D. ditto at 180° C. with 10 per cent. hexane; E. ditto at 180° C. with 10 per cent. benzene vapour.

A set of experiments was carried out to determine the amount of oxidation that would occur in carbon disulphide—air mixtures during twenty seconds' heating at different temperatures; the results so obtained indicate the temperature coefficient of oxidation.

The gas mixtures were passed through a glass tube, 12 mm. diameter, heated in an electric furnace, the rate of flow being adjusted to allow approximately 20 seconds' heating at the required temperature. The exit gases were analysed in order to determine the amount of oxidation. The results are shown in Fig. 3, from which it will be seen that the rate of depletion of oxygen in the mixtures was small and increased slowly over a wide range of temperature until the temperature of self-ignition was approached. The remarkable effect of mixture strength on the oxidation behaviour of carbon disulphide in air and on its temperature of self-ignition is again shown. The behaviour of normal heptane and of ethyl ether vapour in air under similar conditions was studied for purpose of comparison and it will be seen that the temperature coefficients of oxidation are high in the neighbourhood of 300° below which little or no oxidation occurs during the 20 seconds'

heating. The influence of mixture strength too was found to be considerably smaller.

The significance of the temperature coefficient of oxidation with regard to detonation has been discussed by Tizard and Pye.[12] They showed that from measurements of the rate of loss of heat just below the ignition temperature by adiabatic compression and of the intervals between the end of compression and the occurrence of ignition at different temperatures it is possible to deduce the temperature coefficient of the gaseous reaction. Their results showed that the temperature coefficient of the combustion of carbon disulphide is much lower than that of heptane or ether which have strong pro-knock tendencies in an internal combustion engine.

The surprisingly small temperature coefficient of the oxidation of carbon disulphide and the marked influence of mixture strength on the results call for some comments.

Usually, the volume changes during oxidation at constant temperature cease after a few hours, becoming smaller and smaller with time in all instances, although the oxygen is not depleted to such an extent that the mixture cannot be ignited by applying a flame. This behaviour suggests that the products of oxidation act as inhibitors of oxidation and evidence on this point was obtained. H. B. Dixon,[13] has found that sulphur dioxide exerted a considerable inhibitory action on the self-ignition of carbon disulphide mixtures and that if a mixture failed to ignite in his concentric tube burner the power of inflammation was restored by a prolonged sweeping out of the cylinder. During the slow oxidation of carbon disulphide besides small amounts of sulphur dioxide, carbon oxy sulphide, etc., a brown solid is formed which settles on the walls of the bulb and this possibly can contribute to the inhibition of the oxidation both by covering the active surface of the glass and by actual inhibitory action. Experiments were carried out to determine whether this inhibitory action by the dark brown film occurred and to what extent. The pressure differences in a mixture contained in a bulb coated with the deposit from a previous experiment were compared with those in a clean bulb but the inhibitory effect, fairly marked at first, became less noticeable with time due to the accumulation of the deposit on the walls of the clean bulb.

Analyses were made of the contents of some of the bulbs after heating for some time; small amounts of sulphur dioxide and carbon oxy sulphide were found to be present and to accumulate towards the end of the reaction. The rate of oxygen absorption was relatively high at the beginning of the oxidation and diminished with time, as shown in Fig. 4. Brunner[14] estimated the rate of depletion of oxygen during the slow combustion of hexane vapour in oxygen and found that after about 20 minutes almost the whole of the oxygen had disappeared. With the carbon disulphide mixtures, however, there was a considerable proportion of oxygen remaining even after several hours.

Action of Inhibitors.—The marked action of nitrogen peroxide, hexane and benzene vapour, shown in Fig. 4, in reducing the rate and amount of oxygen absorbed, bears out in a striking manner the inhibitory action of these substances on the phosphorescence and slow oxidation of carbon disulphide vapour,[10] and in raising the self-ignition temperatures,[13] and reducing flame speed.[15]

The lower rate of depletion of oxygen in the presence of inhibitory substances is accompanied by smaller volume changes, as would be expected.

[12] Phil. Mag., 1926, 1094 : 1922, 79.   [13] Rec. trav. Chim., 44, 305, 1925.
[14] Helv. Chim. Acta., 2, 56, 1928.   [15] White, J.C.S., 751, 1928.

In the presence of very small amounts of an inhibitory substance, such as hexane vapour, it is possible to follow volume changes over a long period of time in a weak gas mixture which normally self-ignites. Pressure results obtained by the addition of the vapour of hydrocarbons, etc., to a carbon disulphide-air mixture at various temperatures are shown in Figs. 5 and 6.

(a) 4 per cent. CS_2 in air at 120° C.
A. With 1 per cent. benzene.
B. „ 0·5 per cent. alcohol.
C. „ 0·2 per cent. nitrogen peroxide.

(b) 4 per cent. CS_2 in air at 180° C.
A. With 1 per cent. benzene.
B. „ 0·5 per cent. ethyl alcohol.
C. „ 0·5 per cent. methyl alcohol.

FIG. I., 5.—The oxidation of carbon disulphide vapour in air. Action of inhibitors on volume changes with time.

(a) 10 per cent. CS_2 in air at 180° C.
A. With 2 per cent. hexane.
B. „   „   cyclohexane.
C. „ 2·5 per cent. acetone.
   Chain line—no inhibitor added.
D. With 1·2 per cent. isopentane.
D. 1. With 0·5 per cent. isopentane.
E. With 0·2 per cent. iron carbonyl.

(b) 30 per cent. CS_2 in air at 180° C.
A. With 15 per cent. benzene.
A. 1. With 2 per cent. benzene.
B. With 10 per cent. ethyl alcohol.
C. „ 2 per cent. hexane.
D. „   „   amyl nitrite.

FIG. I., 6.—The oxidation of carbon disulphide vapour in air. Action of inhibitors on volume changes with time.

The marked effect of small amounts of anti-oxygens in suppressing oxidation in weak mixtures, however, is not so evident with richer mixtures; thus, an addition of 1 per cent. benzene vapour to a 4 per cent. carbon disulphide-air mixture causes a considerable suppression of oxidation at 180°, but the inhibitory effect of this amount is small with a 37 per cent. carbon disulphide-air mixture at 180° and at higher temperatures becomes less so. Iron

carbonyl appeared to have little effect in suppressing oxidation, a result in keeping with observations of the weak action of iron carbonyl in suppressing phosphorescence.

Some substances such as amyl nitrite or nitrogen peroxide have a strong action in stopping self-ignition and phosphorescence but do not decrease the volume change whilst hexane, alcohol and some other substances can at higher temperatures, apparently cause a diminution in volume which is followed by an increase. Results illustrating this behaviour are shown in Fig. 7.

Autoxidation. — The behaviour of benzene, etc., in inhibiting oxidation yet causing no diminution in volume is of extreme cogency to the theory of combustion in general. It is a proof of the formation of activated peroxides which cause the autoxidation of benzene to phenol, or of the alcohols, coal gas, etc., to water and carbon dioxide at temperatures when normally they remain unoxidised. The multiplication of molecules due to autoxidation of the inhibitor is responsible for the increase in volume.

Chain line—35 per cent. CS_2 in air at 325°.
A. Ditto with nitrogen peroxide.
B. ,, with amyl nitrite vapour.
C. ,, with methyl alcohol vapour, 10 per cent.
D. ,, with benzene vapour, 10 per cent.
E. ,, with hexane vapour, 10 per cent.

FIG. I., 7.—The oxidation of carbon disulphide vapour in air with addition of benzene vapour, etc. Volume changes with time.

The presence of phenol in the combustion products was demonstrated by bubbling the gases through dilute bromine water when the tribromo-
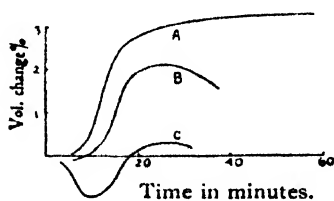
FIG. I., 8a.—The oxidation of ethyl alcohol in the presence of carbon disulphide at 225° C.

A, 10 per cent. ethyl alcohol vapour in air; B, ditto with equal volume of 10 per cent. carbon disulphide vapour in air at 225°; C, ditto at 250°.
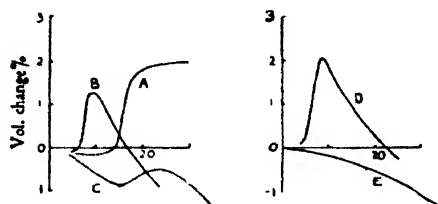
FIG. I., 8b.—The oxidation of hexane in the presence of carbon disulphide.

A, Hexane vapour in air at 256°; B, ditto with equal volume of carbon disulphide vapour in air (15 per cent. mixture strength) at 282°; C, ditto at 275°; D, Hexane vapour in air with equal volume of carbon disulphide vapour in air (33 per cent. mixture strength) at 297°; E, ditto at 290°.

phenol derivative was precipitated and could be crystallised. Similarly with alcohol vapour or coal gas the condensation of water on the cold ends

of the combustion tube indicated the autoxidation of these organic substances.

When ethyl alcohol vapour is heated in air alone the oxidation changes with time can be followed by means of a pressure increase instead of a decrease found with carbon disulphide. With a mixture of alcohol and carbon disulphide, the pressure changes on heating are not the algebraic mean but the results indicate that the alcohol inhibits the oxidation of carbon disulphide, which, in turn, appears to decrease slightly the oxidation of the alcohol. This behaviour is shown in Fig. 8 obtained with mixtures in equal volumes of carbon disulphide with alcohol and hexane vapour respectively.

Action of Surfaces.—Surface effects were found to play an important part in the oxidation of carbon disulphide vapour. Some surfaces such as glass, porous pot, etc., increased the rate of oxidation, whilst metallic surfaces had an inhibitory action, but in all instances the surfaces became gradually coated with the dark-brown deposit formed during the oxidation of the carbon disulphide and the various effects became less. Powdered glass, porous pot, and silica (ppd.) were added each in turn to the reaction bulb and the rate of oxidation compared with that of the mixture in a plain bulb by means of pressure differences. During the first few minutes the rate of oxidation was greater with the additions but the rate rapidly became normal as the coating of dark-brown deposit accumulated. Sulphur dust, powdered electrode carbon and vanadium pentoxide had a slight inhibitory action at lower temperatures, the effect being less noticeable at higher temperatures.

A, carbon disulphide alone; B, in presence of copper; C, in presence of iron; D, with addition of 5 per cent. benzene vapour.

FIG. I., 9.—The effect of metal surfaces and benzene vapour on the rate of oxidation of carbon disulphide vapour at different temperatures.

Metallic surfaces had a strong inhibitory action on the initial oxidation, a result in keeping with the raising of self-ignition temperatures by the presence of metal foils and gauzes.[10] Copper and iron surfaces inhibited strongly; aluminium had a weak effect and chromium a moderate effect.

Some results showing the action of copper and other inhibitors on the rate of oxidation of carbon disulphide vapour in air are shown in Fig. 9.

(*b*) The Oxidation in Air of Carbon Monoxide.

The oxidation of carbon monoxide is of particular interest to the subject of engine detonation since it is known that carbon monoxide is formed to some extent during the oxidation of fuel vapours, prior to carbon dioxide, and is capable of exerting an inhibitory action. It is feasible that pure aldehydes which do not promote engine detonation although they are easily oxidisable with chemiluminescence owe in part their relatively low rate of oxidation and low temperature coefficient of gaseous reaction to the intermediate formation of the inhibitor, carbon monoxide, by thermal decomposition of the aldehyde,

$$CH_3CHO \rightarrow CO + CH_4.$$

It will be remembered that Faraday reported that a small quantity of carbon monoxide inhibited the combination of hydrogen and oxygen.

The experiments described in this paper were carried out mainly with a view to determining the extent of the inhibitory action of carbon monoxide and of ascertaining the temperature coefficient of oxidation and the influence of various surfaces and vapours upon it. The apparatus used was the same as with the carbon disulphide experiments, and carbon monoxide saturated with water vapour at $12°$ was used.

It will be seen from Fig. 10 that below $450°$ little or no oxidation occurs during 20 seconds' heating in a hard glass tube of 12 mm. diameter. At $677°$ a 25 per cent. mixture was found to self-ignite in the tube. Dixon has given a self-ignition temperature of $651°$ for a mixture of moist carbon monoxide in air, and Mallard and Chatelier have given the value $650°$ to $657°$ for a mixture of 30 per cent. carbon monoxide in oxygen.

The oxidation results were found to be dependent to some extent upon the glass ware employed; some bulbs and tubes although of the same size and from the same stock were a little more reactive. The reaction rates were also found to be less in larger bulbs so for the purpose of comparing the influence of various metallic surfaces and hydrocarbon vapours, etc., on the oxidation results the same glass tube and bulb were employed.

Temperature Co-efficient of Reaction.—A mixture in air of 18 per cent. carbon monoxide, saturated with water vapour at $12°$, was passed through the glass tube at such a rate that the time of heating was approximately 20 seconds, and the exit gases were analysed. The amount of carbon dioxide was small until a temperature of $600°$ was approached. With further rise of temperature above $600°$ the rate of oxidation increased, at first slowly and then rapidly when above $625°$, until self-ignition occurred at about $680°$. The curve relating the amount of oxygen depletion with temperature resembles that for carbon disulphide and is different from that for a pro-knock hydrocarbon such as normal heptane (see Figs. 3 and 10).

A, carbon monoxide alone in air; B, with 10 per cent. addition of methane; C, oxidation of carbon monoxide in presence of copper.

FIG. I, 10.—The oxidation of carbon monoxide in air under different conditions (tube experiment).

The inhibitory influence of the addition of 10 per cent. methane on the oxidation results of the mixture is shown by the displacement of the curve in the direction of higher temperature by nearly $80° C$. The self-ignition temperature was raised and the rate of oxidation increased a little less with temperature than without the methane. Copper exerted a marked influence on the oxidation results; oxidation began appreciably below $400°$ and self-ignition was delayed so that the temperature coefficient of gaseous reaction was strongly decreased by the presence of copper, the surface area of which was about the same as that of the glass walls of the tube. Iron, lead, and nickel exerted a similar effect on the oxidation behaviour whilst aluminium and magnesium did not cause much change.

The experiments with carbon monoxide were repeated using the bulb method when the time of heating was extended to over an hour under isothermal conditions.

The rate of reaction was slow at temperatures below 600° and could be followed over several hours. Results obtained with a glass bulb, which appeared to be more reactive than usual, are shown in Fig. 11; the rate of volume decrease was irregular and did not increase very much with rise of temperature; a similar behaviour was experienced with carbon disulphide-air mixtures. When a small piece of metal was introduced into the tube the rate was appreciably increased and results obtained by adding different amounts of copper and lead foil to the reaction bulb are shown in Fig. 12.

Pressure change in cms. Toluene.

(a) 10·4 per cent. mixture strength.
(b) 15·7 „   „   „
(c) 52   „   „   „
(d)   I. 25 per cent. mixture in 1 in. diameter bulb, 400° C.
      II.   „   „   „   3 in.   „   „   „
     III. 25 per cent. mixture with an addition of 20 sq. cms. of iron foil.
      IV. 25 per cent. mixture with an addition of 10 sq. cms. of copper foil.
       V. 25 per cent. mixture with an addition of 10 sq. cms. of tin foil.

FIG. I., 11.—The oxidation of carbon monoxide in air, under different conditions (bulb method).

Aluminium, zinc, antimony, and magnesium were tried but these did not exert much effect.
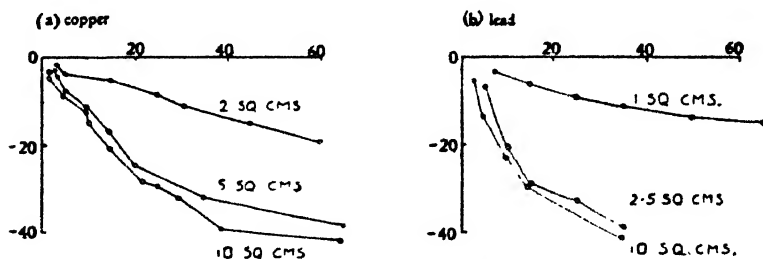
FIG. I., 12.—The influence of metal surfaces on the combustion of carbon monoxide (bulb experiments).

Autoxidation of Carbon Monoxide.—Although carbon monoxide did not usually undergo oxidation at temperatures much below 400° in glass, it could be demonstrated that oxidation of carbon monoxide takes place appreciably at low temperatures in the presence of hydrocarbons, etc., undergoing oxidation. So whilst the carbon monoxide was exerting an inhibitory action it was being autoxidised. A cyclohexene vapour-air mixture was found at 297° to give a sudden pressure rise after an induction period of nearly ten minutes; when about 7 per cent. carbon monoxide

was added to the cyclohexene-air mixture there was a considerably less pressure rise and its time was delayed whilst a subsequent steady fall in pressure was traced by analysis of the gases to the conversion of the carbon monoxide into carbon dioxide. These results are shown in Fig. 13.

The influence of carbon monoxide on the oxidation of carbon disulphide in air is interesting. It has been found previously that when carbon monoxide was added to a carbon disulphide-air mixture emitting a glow in a hot tube that the chemiluminescence brightened and extended.[10] By following the pressure change it was concluded that the carbon monoxide at first underwent autoxidation since the volume decrease was at first greater with the carbon monoxide present. Experiments were carried out by comparing the pressure changes in the mixtures with and without the addition of carbon monoxide by noting the differential pressure in the bulb apparatus described. These results obtained with carbon disulphide are shown in Fig. 13 (b).

With carbon disulphide and cyclohexene vapour in air mixtures each containing carbon monoxide there was an initially

FIG. I., 13.—The influence of carbon monoxide on the oxidation of (a) cyclohexane (297° C.), (b) carbon disulphide (300° C.), (c) hexane, and (d) cyclohexene (bulb experiments).

greater fall in pressure due to the autoxidation of the carbon monoxide, whilst with normal hexane at 256° the presence of carbon monoxide increased the induction period prior to sudden rise of pressure to about 30 minutes.

The autoxidation of carbon monoxide when added as an inhibitor to hydrocarbon vapours, carbon disulphide, etc., is a strong support to the hypothesis that a primary stage in the combustion of fuel vapours is the formation of an activated complex of a molecule of the fuel with a molecule of oxygen, the complex acting as a catalyst in the oxidation process.

Summary.

1. The oxidation of carbon disulphide vapour and of carbon monoxide in air is autocatalytic in character ; the " moloxide " or primarily formed activated complex of fuel molecule and oxygen molecule performing the rôle of catalyst and controlling the rate of gaseous reaction.

2. The oxidation of both substances is sensitive to the action of inhibitors which by reacting with the catalyst and destroying its peroxide character, lower the rate of reaction and its temperature coefficient and in so doing are autoxidised. Surfaces, especially of metals control the rate of reaction and lower the temperature coefficient of gaseous reaction.

3. Excess of fuel vapours, especially in the case of carbon disulphide favours a lower rate of reaction and lower temperature coefficient so behaving as an inhibitor. The products of slow combustion of carbon disulphide also exert an inhibitory effect.

4. The temperature coefficient of gaseous reaction of both carbon disulphide and carbon monoxide in air is relatively small compared with that of the paraffin hydrocarbons. This is in accord with the conclusion of Tizard and Pye (*Phil. Mag.*, 1922, 79) that anti-knock properties of fuel vapours are associated with a low temperature coefficient of slow combustion.

II. THE OXIDATION OF (a) HYDROGEN, (b) METHANE, AND (c) COAL GAS IN AIR.

Hydrogen, methane, and coal gas possess high self-ignition temperatures in air and are resistant to oxidation until temperatures approaching or above 600° C. are reached. Concomitant with this high resistance to self-ignition and to oxidation in air, these gases when used as fuel in an internal combustion engine possess anti-knock properties; thus, Ricardo found [1] that using a weak mixture of hydrogen (50 per cent. weak) smooth running of the engine was obtained at 7 : 1 compression ratio with light loads, also when using kerosene the substitution of hydrogen for a part of the kerosene not only ensured the complete combustion of the kerosene but considerably reduced knocking. With the theoretical mixture strength of hydrogen, it was found impossible to run the engine because of violent pre-ignition accompanied by firing back into the carburettor, so the precise H.U.C. ratio for hydrogen has not been determined.

The temperature coefficient of oxidation of pure hydrogen in air is considerably greater than that for methane, but the oxidation rate and its temperature coefficient are lowered considerably by the addition of hydrocarbon vapours and the presence of metallic surfaces·or metal dopes. It appears feasible, therefore, from the standpoint of the conclusion of Tizard and Pye,[2] who found that the anti-knock properties of a fuel are in agreement with the lowness of the temperature coefficient of gaseous reaction for the H.U.C. ratio of hydrogen (without admixture with hydrocarbon vapour) to be considerably below that of methane and not to be so high as might be expected from engine results obtained with hydrogen mixed with hydrocarbon vapours.

The action of inhibitors on the oxidation of hydrogen puzzled Faraday (1834) who, in an account of his sixth series of experimental researches in electricity, wrote a detailed account of the investigation on the combination of electrolytic gas in the presence of platinum foil. He reported that one forty-eighth part of olefiant gas (ethylene) and one-eighth part of carbon monoxide inhibited the combination. A similar inhibitory effect was observed with one-sixteenth to one-twentieth part of sulphuretted hydrogen, phosphoretted hydrogen, carbon disulphide vapour, ether or oil-gas vapour. Faraday stated [3] that the explanation "remains to be decided by more extended experiments," but it is only recently that explanations for the action of inhibitors or of "anti-knocks" have been brought forward after nearly a hundred years.

The following experimental work has been carried out to determine the oxidation rate in air and its temperature coefficient for hydrogen, methane, and coal gas under different conditions.

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[1] *J. Inst. Aut. Eng.*, **18**, 337, 1924.   [2] *Phil. Mag.*, **79**, 1922.
[3] *Phil. Trans. Roy. Soc.*, **124**, 55, 1834.

The peroxide mechanism of combustion is substantiated from the oxidation behaviour of these gases and autocatalysis and autoxidation through peroxides have been demonstrated.

Experimental.

The experimental work involved the use of two methods, *viz.* (*a*) the closed bulb method, by which the gas mixture was maintained at constant temperature in a hard glass bulb and the course of the reaction followed by pressure change, and (*b*) the heated tube method by which the gas mixture was passed through a glass tube heated in an electric furnace and the products of combustion examined. The time of heating was kept at approximately 20 seconds.

A full description of the apparatus and methods has been given elsewhere.[4]

Temperature of Initial Combustion.

The temperature of initial oxidation of the gases in air when the mixtures were passed through the heated glass tube, was manifested by an almost sudden appearance of a fog visible in a bright beam of light; simultaneously, a deposition of dew on the cold exit end occurred and aldehydes in the case of methane and coal gas could be detected. This temperature of initial combustion, T.I.C., the lowest temperature when combustion began as observed by fog formation and dew deposition, varied considerably with mixture strength. This is shown in Table I. (Fig. 1).
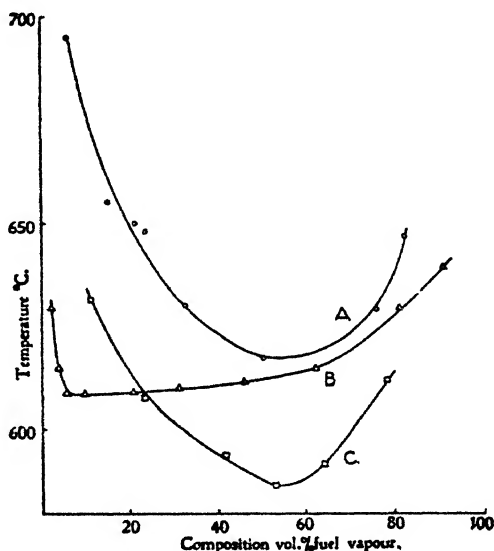
FIG. II., 1.—The temperatures of initial combustion in air of different strength mixtures of (*a*) methane, (*b*) hydrogen, and (*c*) coal gas.

TABLE I.

TEMPERATURES OF INITIAL COMBUSTION OF (*a*) HYDROGEN, (*b*) METHANE, (*c*) COAL GAS IN AIR FOR DIFFERENT MIXTURE STRENGTHS BY THE TUBE METHOD: TIME OF HEATING, 20 SECONDS.

(*a*) Vol. Per Cent. Hydrogen.	T.I.C.	(*b*) Vol. Per Cent. Methane.	T.I.C.	(*c*) Vol. Per Cent. Coal Gas.	T.I.C.
2·1	630	5·5	695	11	631
3·3	615	14	655	22	609
5·7	609	15·7	650	43	595
8·0	610	17·8	648	53	585
21	611	32	630	·63	594
31	611	50	615	79	614
46	612	73·5	629		
61	615	82	647		
81	632				
92	640				

Temperature Coefficient of Oxidation Rate.

Reactions in the gaseous mixtures occurred to some extent below these temperatures of initial combustion when the mixtures were heated for several hours in a glass bulb; the T.I.C.'s. given in Table I. therefore represent a stage when oxidation became noticeable during a period of heating of about 20 seconds. The amount of oxygen depletion in the gas mixture during the 20 seconds' heating at temperatures at and just above the temperatures of initial combustion given is very small, and only at considerably higher temperatures does the reaction proceed to any marked extent; thus, at 622° C. ten degrees above the T.I.C. with a mixture of equal volumes of hydrogen and air, the depletion of the oxygen was less than 5 per cent.

A measure of the oxidation rate is determinable by ascertaining the proportion of oxygen consumed in the mixture during any arbitrary period of time and the temperature coefficient of gaseous reaction is indicated by curves relating the temperature and proportion of oxygen consumed.

Such curves obtained with 20 seconds' heating for hydrogen, methane, and coal gas, are shown in Fig. 2. The curve for hydrogen shows a rapid
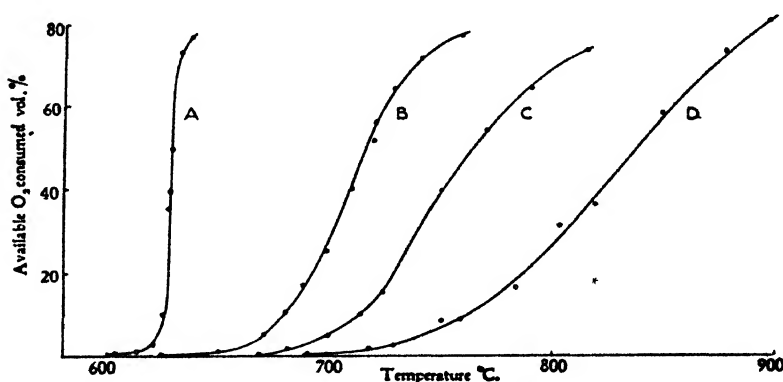
FIG. II., 2.—The rate of oxidation in air of (a) hydrogen, 40 per cent. vol., (b) coal gas, 40 per cent. vol., (c) methane, 40 per cent. vol., and (d) methane, 60 per cent. vol. at different temperatures.

rise in the oxidation rate at about 625°, whereas for coal gas and methane the curves of similar sigmoid shape are considerably less steep, indicating that the temperature coefficient of coal gas is about seven times smaller and methane about ten times smaller than that of hydrogen.

With richer mixtures of methane the temperature coefficient of reaction is still less; this is shown in Fig. 2 where it will be seen that the slope of the curve decreases with increase in richness of the mixture.

In the case of hydrogen at temperatures corresponding to the steep portion of the curve, self-ignition was liable to occur especially with the leaner mixtures. The position of the curve for coal gas is intermediate between that of hydrogen and methane both with regard to temperature and slope; this is to be expected since methane and hydrogen comprise the major portion of coal gas and hydrocarbon vapours exert an inhibitory action on the combustion of hydrogen.

It will be observed from the sigmoid shape of the curves that for an appreciable range of temperature beginning with the temperature of initial combustion that the rate of reaction increases only very slowly with rise of

temperature. It has been suggested that this slow reaction is due to surface reactions.

Although the walls of the glass tube must have played some part in the oxidation (heterogeneous reaction) reaction in the body of the mixture (homogeneous reaction) undoubtedly occurred, but it is difficult to assign any particular portion of the curve to either reaction. It is feasible that both reactions occur simultaneously although perhaps at different rates, the wall effect being possibly more prominent at the lower temperature. Gibson and Hinshelwood[5] considered that the slow reaction occurring in silica and porcelain vessels at lower temperatures between hydrogen and oxygen takes place entirely at the surface; they point out that it is almost independent of pressure. Bodenstein[6] supposed that the combination of hydrogen and oxygen in porcelain tubes occurred entirely at the surface but subsequent workers have shown that combination in the gas phase occurred to a greater extent than Bodenstein had considered.[7]

The following experiments show the great importance of surfaces and inhibitors in altering the temperature coefficient of gaseous reaction and in altering the temperature of initial combustion, the surfaces sometimes behaving in the dual capacity of inhibitor and accelerator.

When the glass tube through which the hydrogen mixture passed was packed with unglazed porcelain little or no difference was observed in the temperature of initial combustion, but the temperature coefficient of reaction was reduced appreciably.

In this respect the porcelain surface behaved as an inhibitor

FIG. II., 3.—The rate of oxidation in air of hydrogen in presence of (a) unglazed porcelain, (b) cyclohexane vapour, (c) benzene vapour, at different temperatures, compared with pure hydrogen.

though it was not so effective as a small proportion of hydrocarbon vapour added to the hydrogen mixture. Fig. 3 illustrates the results obtained for a hydrogen-air mixture with (a) unglazed porcelain, (b) 5 per cent. cyclohexane, and (c) 5 per cent. benzene. The unglazed porcelain reduced the temperature coefficient by about 30 per cent. whilst cyclohexane and benzene reduced it to at least third the value, benzene being a little more efficacious than cyclohexane.

Benzene and cyclohexane were both autoxidised by the active hydrogen peroxides formed during the combustion and phenol could be isolated. The action of the porcelain in reducing the temperature coefficient was presumably a destruction of the activated hydrogen peroxides at the surface whereby the amount of active catalyst of combustion was reduced.

Evidence was obtained by the closed bulb method that reaction occurred in a 10 per cent. hydrogen-air mixture containing 6 per cent. nitrogen

[5] Proc. Roy. Soc., A 119, 591, 1928.   [6] Z. physik. Chem., 29, 665, 1899.
[7] Cf. Rowe, Z. physik. Chem., 59, 41, 1907.

peroxide as low as 175° C. after heating for a few minutes; nitrogen peroxide therefore behaves as a strong accelerator, see Fig. 4. It was found that nitrogen peroxide itself was capable of reacting with hydrogen oxidising it to water so the changes which occur in the mixture are complicated by this additional reaction.

The inhibitory action of benzene on the oxidation of methane was not clearly demonstrated since above 700° C. benzene itself undergoes oxidation in air. The inhibitory action of lead tetra ethyl on methane which resembled that of metallic lead could be determined, however. The influence of metals on the oxidation behaviour was studied and it was found that though metals behaved as a catalyst in as far as they reduced the temperature of initial combustion, yet the temperature coefficient of reaction was reduced. The significance of this fact will be realised when it is considered that the metal dopes such as iron carbonyl which behaved similarly to the metal delay detonation in an engine. It appears, therefore, that the temperature coefficient of gaseous reaction is of primary importance with regard to the anti-knock properties of a fuel and not when oxidation begins. This is exemplified in the case of carbon disulphide which though of low self-ignition temperature yet 'possesses a very low temperature coefficient of oxidation and has a definite anti-knock action.

The results of the action of metals and metal dopes on the oxidation behaviour is given in Figs. 5 and 6.

Fig. II., 4.—The oxidation of hydrogen in air (45 per cent. mixture strength); volume decrease with time (a) in the presence of copper at 330°, (b) with 5·5 per cent. nitrogen peroxide; at 250° and (c) with 15 per cent. nitrogen peroxide; at 250°.

The addition of iron and copper gauze to the heating tube lowered the temperature of initial combustion of both hydrogen and methane in air by about 200° C., copper being more effective in this respect than iron. At 450° a 50 per cent. methane-air mixture in the presence of coppergauze showed signs of change when heated in a glass bulb for an hour, but with a few seconds' heating no change could be detected until 500° was approached. The temperature coefficient of oxidation was also lowered considerably in both hydrogen and methane, copper being more effective than iron. Thus, copper reduced the temperature coefficient for hydrogen to about one-eighth of the original value whilst iron reduced it to about one-fourth.

A similar behaviour was experienced with iron and copper gauze in the case of methane which indicates the similarity of the mechanism of combustion of hydrogen with the hydrocarbons, presumably through peroxide formation.

The inhibitory action of benzene in the presence of metal foils is exemplified by the rise in temperature of initial combustion by about 100° C., the temperature coefficient being only slightly altered. Amyl alcohol vapour was found to inhibit the oxidation of hydrogen but to a less extent than benzene, the curve relating oxygen depletion with temperature being shifted about 30° higher instead of 100° as in the case of benzene. On the other hand, ethyl nitrate vapour acted as an accelerator and shifted the curve down the temperature axis by about 10°.

It will be seen from Figs. 5 and 6 that the effect of iron carbonyl on the oxidation rates and temperature coefficients was closely similar to that of
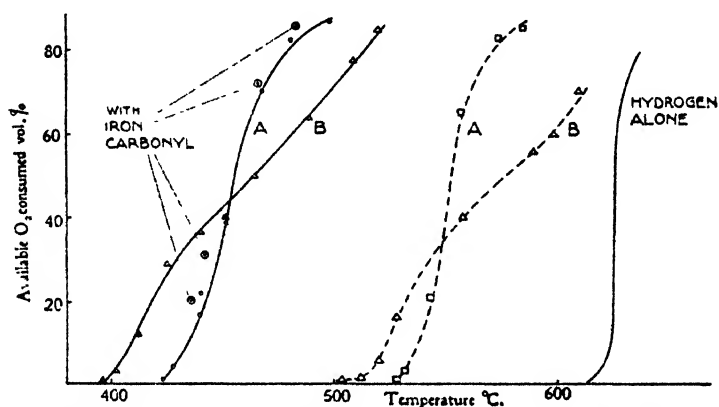
FIG. II., 5.—The influence of (a) iron and (b) copper on the rate of oxidation of hydrogen in air; chain lines—with 10 per cent. addition of benzene vapour.
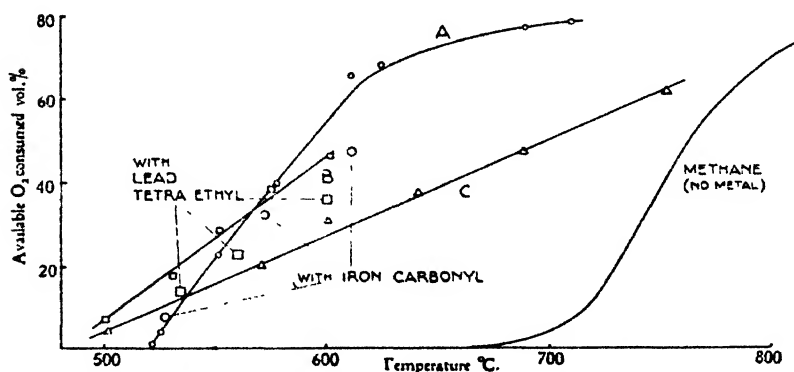
FIG. II., 6.—The influence of (A) iron, (B) lead, and (C) copper on the rate of oxidation of methane in air.

the iron gauze; a similar behaviour was found with lead tetra ethyl and molten lead. These results confirm the view that it is the metal alone of the organometallic compound which is responsible for the anti-knock action, the metal being liberated from the metal compound by thermal decomposition.

· The influence of the metals and metal dopes was marked in diminishing the yields of aldehyde and active oxygen produced normally from the combustion of methane. Hydrogen peroxide in the case of the combustion of

hydrogen was also considerably diminished. Although the yield of active oxygen and aldehydes is diminished with a corresponding increase in the yield of carbon dioxide and water, there is no reason to suppose that the course of combustion is different but rather it appears that the metal surfaces crowd together and hasten the intermediate reactions so that only the final products of combustion are isolated.[8] At 730° the amount of carbon dioxide obtained during the slow combustion of methane in presence of copper was 11 per cent. compared with 0·5 per cent. without copper.

Function of Primarily Formed Peroxides.

Previous workers have indicated to some extent the autocatalytic character of the combination of hydrogen or methane with oxygen and have pointed out the function that primary peroxides can play. Thus, Wartenberg and Sieg[9] stated that they have proved the correctness of the assumption that reaction between two substances is preceded by the formation of an unstable additive compound (a moloxide or primary peroxide) in the cases of both hydrogen and methane. They consider the combustion of hydrogen to proceed through the formation of hydrogen peroxide and of methane through the moloxide $CH_4(O_2)$.

Bach (1897) concluded that hydrogen formed the higher peroxide $H_2(O_2)_2$, a tetroxide, during combustion and demonstrated the presence of peroxides in the combustion products of hydrocarbons.[10]

There are good reasons for assuming that the rate of chemical change in a gaseous mixture is not proportional to the relative numbers of molecules capable of entering into the reaction but is a function of the number of activated molecules which might form only a small proportion of the whole.

Assuming therefore that the rate of combustion is proportional to the concentration of active peroxides or moloxides any factor tending to reduce the number of active centres correspondingly reduces the rate of oxidation. Inhibitors such as benzene vapour, act by reducing the active peroxides which simultaneously autoxidise the benzene to phenol whilst surfaces presumably de-activate and reduce the active peroxide molecules.

Gibson and Hinshelwood[11] consider that the retardation in the oxidation of hydrogen in oxygen is due either to the destruction by a surface decomposition of something which catalyses the principal reaction or to the interruption of reaction chains.

A considerable amount of work has been done by Bone and collaborators on the relative catalysing powers of surfaces towards mixtures of various combustible gases and oxygen, but no definite theory of the mode of action has been propounded; they state that they remain still much in the dark as to its true cause, since catalytic combustion is too complex a phenomenon and its experimental investigation full of pitfalls for the unwary. Much further patient research will be needed before everything is understood.[12]

Professor Bone has lately called attention to the finding of methyl alcohol in the products of the reaction of methane and oxygen at high pressure and considers it a proof of the primary formation of alcohols from

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[8] *Cf.* Campbell, *J. Soc. Chem. Ind.*, **48**, 93, 1929.   [9] *Ber.*, **53**, 2192, 1920.
[10] *Comptes rendus*, **124**, 95, 1897.   [11] *Proc. Roy. Soc.*, **119**, 591, 1928.
[12] " Flame and Combustion in Gases," Bone and Townend, 1927.

hydrocarbons during combustion.[13] According to the peroxide theory methyl alcohol is not the primary product of oxidation but results from the autoxidation of a methane molecule by its moloxide or by intramolecular change of a dimoloxide according to the following equation :—

$$CH_4 + O_2 = CH_4(O_2)$$
$$CH_4(O_2) + CH_4 = 2CH_3OH$$
$$CH_4(O_2) + CH_4 = CH_4(O_2)CH_4 = 2CH_3OH.$$
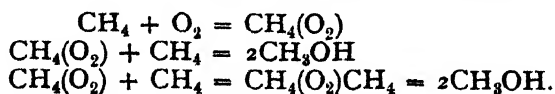
Autoxidation appears therefore to play a principal part in the combustion of methane.

It is possible that the primary peroxide or moloxide is methyl hydrogen peroxide formed by the inclusion of the oxygen molecule between carbon and hydrogen according to the equation,[14]

$$CH_4 + O_2 = CH_3OOH$$
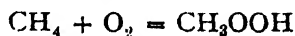
According to the researches of Rieche and co-workers [15] methyl hydrogen peroxide by decomposition yields methyl alcohol in relatively large yields together with hydrogen, formic acid and formaldehyde; similarly its derivative with formaldehyde yields methyl alcohol.

Conclusions.

1. The temperature coefficient of oxidation of methane, of coal gas and of a mixture of hydrogen with a small proportion of hydrocarbon vapour is low. This is in agreement with the conclusion of Tizard and Pye that anti-knock fuels possess a low temperature coefficient of gaseous reaction.[16] Methane is exceptionally resistant to oxidation in air and the mechanism of combustion appears to be through autoxidation in accord with the peroxide theory of combustion ; the primary oxidation product is presumably methyl hydrogen peroxide which yields formaldehyde, methyl alcohol, etc., by decomposition.

2. The temperature coefficient of oxidation of pure hydrogen is relatively high and considerably greater than that for mixtures with hydrocarbon vapours such as that of benzene which acts as an inhibitor. This result suggests that the H.U.C. ratio of pure hydrogen is much lower than might be expected from engine results already obtained with hydrogen and hydrocarbon mixtures.

3. The effect of inhibitors and metal surfaces on the temperature coefficient of oxidation has been studied. In every case the temperature cofficient has been reduced by inhibitors and surfaces and also the peroxide content of the products of gaseous reaction has been found to be reduced so indicating the close relationship between peroxide content, the temperature coefficient of oxidation and the tendency to detonation.

4. The action of iron carbonyl and lead tetra ethyl on the temperature coefficient was found to be almost identical with that of the respective metals confirming the view that the efficiency of metallic compounds as inhibitors is due to the metal portion of the dope liberated during thermal decomposition.

[13] *Nature*, **127**, 481, Mar. 28th, 1931.
[14] *Cf.* Callendar and Mardles, *Engineering*, 4th Feb., 1927.
[15] *Ber.*, **62**, 2460, 1929.   [16] *Phil. Mag.*, 79, 1922.

III. COMPARATIVE STUDY OF THE VAPOUR PHASE OXIDA-
TION IN AIR OF (a) ETHANE AND ETHYLENE, (b) PEN-
TANES AND AMYLENES, (c) ETHYL ALCOHOL AND AMYL
ALCOHOL, (d) ACETALDEHYDE AND VALERALDEHYDE.

A comparative study of the oxidation characteristics of the above sub-
stances has a special bearing on the subject of knocking in the internal
combustion engine and on the theory of combustion in general.   Ethane
and normal pentane are representative of the normal paraffin hydrocarbons,
which are of relatively low anti-knock value whilst ethylene and the amylenes
are members of the olefine series of hydrocarbons, which possess relatively
high anti-knock properties.
It is feasible that the mechanism of combustion of ethane and ethylene
of simple molecular composition would be less complicated than that of the
larger molecule hydrocarbons usually present in motor fuels although the
general mode of oxidation is presumably the same; the results of oxidation
obtained with ethane and ethylene in air should therefore help to decide
the merits and failings of various hypotheses which have been proposed for
the course of the oxidation of hydrocarbons and to throw considerable
light on the causes why certain hydrocarbons induce knocking in an engine.
Experiments on the alcohols (of high anti-knock value) and on the
corresponding aldehydes were included because of the Armstrong-Bone
hydroxylation hypothesis which postulates the primary formation of alcohols
during hydrocarbon combustion.   Bone contends that the aldehydes formed
intermediately from hydroxylated compounds are responsible for engine
detonation,[1] but it has been shown that aldehydes when used as engine fuel
do not promote knocking in an engine, and so the cause of knocking must
be sought in the formation of an unstable prior compound, viz., an activated
moloxide or peroxide.[2]
Aldehydes were formed in profusion during the slow combustion of the
hydrocarbons of both classes and also from the combustion of the aldehydes,
but it was found that the alcohols were not readily oxidisable during a short
time of heating, and the proportion of aldehydes in the oxidation products
was small.   In short the oxidation characteristics of alcohols are distinctly
different from those of hydrocarbons, a behaviour which is hardly to be
expected if according to the hydroxylation hypothesis the first tranformation
of a hydrocarbon during oxidation is to an alcohol.
Similarly it can be shown that the oxidation characteristics of ethylene
are decidedly different from those of ethane ; this is at variance with the
hypothesis that the first transition during the oxidation of a saturated hydro-
carbon is the loss of hydrogen and the formation of the corresponding
olefine hydrocarbon which is subsequently oxidised.[3]   Pope, Dykstra, and
Edgar [4] consider that the first transition in the combustion of a saturated
hydrocarbon is an aldehyde, the reaction proceeding by a chain mechanism.
This view is not confirmed by the study of aldehyde combustion which
is distinct in many ways from that of hydrocarbon combustion.
It would appear from the oxidation results obtained with fuel vapours
that any satisfactory theory of combustion must account for the auto-
catalytic character and also for autoxidation which occurs to a major extent.

[1] Bone and Hill, Proc. Roy. Soc., 129, 434, 1930.
[2] Callendar and Mardles, Engineering, 4th Feb., 1927.
[3] Lewis, J.C.S., 1555, 1927 ; 759, 1929.
[4] J. Amer. Chem. Soc., 51, 1875, 2203, 2213, 1929.

The peroxide theory of combustion which postulates the primary formation of an activated peroxide, a complex of a fuel molecule with an oxygen molecule, has been borne out by results of this investigation, the activated peroxide or moloxide acting as a catalyst and autoxidator.

The composition of the moloxide is presumably an alkyl hydrogen or dialkyl peroxide formed by the entry of the oxygen molecule between the C and H in a CH group or C and C in a CC Group respectively :

$$H_3C\ CH_3 + O_2 \nearrow \begin{array}{l} H_3C\ CH_2\ OOH \\ \\ H_3COOCH_3 \end{array}$$
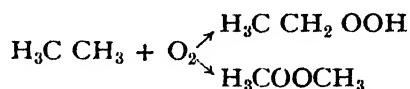
In the case of amylene or ethylene it is possible that a similar oxidation occurs, the oxygen not necessarily adding on to the double bond. Pope, Dykstra, and Edgar [4] have pointed out that the olefine hydrocarbons are not always attacked at the double bond but at the end, a finding in favour of the formation of alkylene hydrogen peroxides.

Experimental.

Experiments were carried out by two methods : (a) the flow or tube method whereby the mixture of hydrocarbon and air was passed through a heated glass tube allowing a time of heating of about 20 seconds, and (b) manometric or closed bulb method when the mixture was maintained at a constant temperature and pressure measurements taken frequently, also analytical tests were carried out from time to time. A full description of the methods has been given in previous reports in this series.

The experimental results obtained show that ethylene and the amylenes begin to oxidise in air at lower temperatures than ethane and the pentanes respectively, but the temperature coefficient of gaseous reaction is less with the unsaturated hydrocarbons. In Table I., Fig. 1, are given temperatures of initial combustion (T.I.C.) when the mix-

FIG. III., 1.—The combustion of (A) Ethane and (B) Ethylene.

tures gave the first signs of oxidation, viz., by fog formation and deposition of dew, etc., on the cold exit end of the hot glass tube; the time of heating was approximately 20 seconds. With increase in richness of the mixtures the temperature of initial combustion fell but eventually rose again.

TABLE I.—THE TEMPERATURES OF INITIAL COMBUSTION OF (a) ETHYLENE,
(b) ETHANE IN AIR; DIFFERENT MIXTURE STRENGTHS.

(a) Ethylene in Air.

Mixture strength (% volume)	1·9	3·0	5·4	7·5	18	24	31	37	43	56	64	78
T.I.C. (°C)	540°	535°	530°	515°	505°	490°	480°	464°	459°	453°	465°	468°

(b) Ethane in Air.

Mixture strength (% volume)	6·8	16·7	20	22	27·3	49	50	54
T.I.C. (°C.)	590°	575°	565°	560°	555°	545°	545°	542°

The corresponding T.I.C.'s for ethyl alcohol and iso pentane, etc., have been given previously,[2] and for amylene, acetaldehyde, etc.[5]

The lowest T.I.C. for amylene by the hot tube method was 257° for a 40 per cent. mixture whilst for *n* pentane the lowest temperature noted was about 285°. The alcohols by this method gave considerably higher results than the corresponding paraffins, thus with ethyl alcohol the observed minimum T.I.C. was above 450°. It will be shown subsequently that the alcohols oxidise slowly and have a low temperature coefficient of oxidation, and although oxidation was not detected by the tube method until higher temperatures were reached, evidence of oxidation at lower temperatures was obtained by the bulb method when the time of heating was many minutes or hours.

This behaviour apparently explains the contradictory statements that alcohol is readily oxidised[6] and that alcohols are oxidised only with difficulty.[7]

The aldehydes gave relatively low T.I.C.'s, viz. 185° for acetaldehyde and 230° for valeraldehyde, but it was found that they were oxidised relatively slowly in air and the temperature coefficient of gaseous reaction was small.

Temperature Coefficient of Gaseous Reactions.
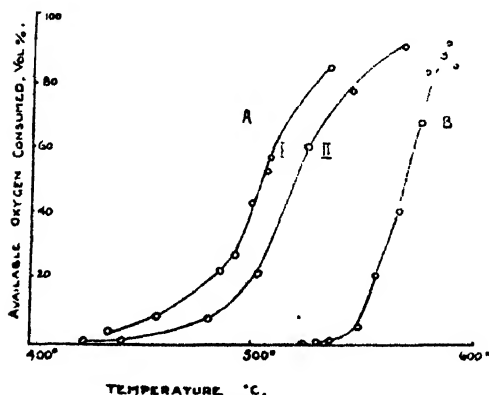
FIG. III., 2.—The rate of oxidation in air at different temperatures of (A) Ethylene, I 20 per cent., II 43 per cent. mixture, and (B) Ethane.

The rate of gaseous reaction at any particular temperature was obtained by determining the amount of oxygen depletion after a time of heating of about 20 seconds whilst the gas was streaming steadily through the heated glass tube. The temperature coefficient of gaseous reaction was obtained by determining the variation in this rate with temperature change and is readily indicated by the slope of the curve relating values for oxygen depletion with the temperature.

[5] Gill, Mardles, Tett, *Trans. Faraday Soc.*, 574, 1928.
[6] Bone and Stockings, J. C. S. 85, 719, 1904.
[7] Layng and Youker, *Ind. Eng. Chem.*, 20, 1048, 1928.

It will be seen from Fig. 2 that the curve obtained with an ethane-air mixture is decidedly more steep than those for ethylene, being approximately 50 per cent. greater, although the sigmoid character of the curves is common to all but less pronounced with ethane. A similar behaviour is found with the pentanes and amylenes respectively (see Fig. 8).

Oxidations at Low Temperatures.

Closed bulb experiments were carried out at temperatures considerably lower than the temperatures of initial combustion found by the tube
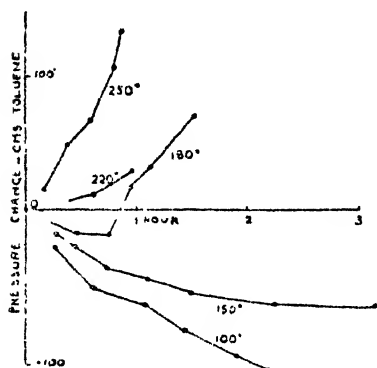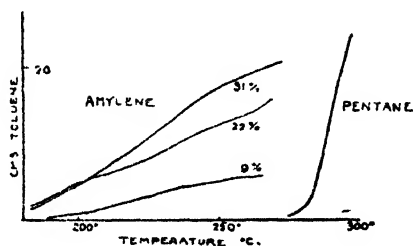
Fig. III., 3.—Pressure changes during the oxidation of amylene.

method. After several hours' heating at 490° a gradual but very slight absorption of oxygen occurred with an ethane-air mixture. Ethyl nitrate hastened and increased the absorption whilst hydrochloric acid gas decreased it. Ethylene showed signs of oxidation at about 400° C.; after two hours' heating at 410° half of the oxygen had become depleted. Amylene vapour in air is oxidisable at 100° there being a slight diminution in volume; at higher temperatures the oxidation changes were found to be accompanied by an increase in volume. This is shown in Fig. 3a, the results being obtained with the bulb method for amylene vapour in air, mixture strength 10 to 31 per cent. and with a temperature range of 100° to 250°.

The pentanes on the other hand showed little or no change below 250°, but when the reaction set in it did so rapidly. This difference in behaviour is also shown in Fig. 3b when the pressure rise was noted when the temperature was raised at about 1° per minute. Amylene-air mixture gave a gradual increase in pressure whereas a pentane-air mixture showed a nearly sudden rise beginning at about 280°.

The alcohols and acetaldehyde were found to behave similarly to amylene by these methods indicating lower temperature coefficients of slow combustion than either ethane or pentane.[5]

The Action of Inhibitors.

When methyl and ethyl alcohol and benzene vapour were added to an ethylene-air mixture undergoing slow combustion no decided change in the rate of oxidation was observed, but phenol, iron carbonyl and lead tetra ethyl as well as metal surfaces did, however, exert a strong action in lowering the temperature coefficient of gaseous reaction. The action of lead tetra ethyl was similar to that of lead confirming the conclusion that it

is the metal portion of the organo metallic dopes which is responsible for the anti-detonating action. Some results are shown in Fig. 4 from which it will be noticed that the metals lowered the temperature of initial combustion considerably, in this respect behaving as a catalyst, yet by reducing the temperature coefficient an inhibitory action was exerted.

With ethane iron was found to be more effective than copper whereas with ethylene the reverse behaviour was found; aluminium had little or no effect on the temperature of initial combustion of ethylene but lowered that of ethane by 65° C. These differences are important to the theory of the mechanism of combustion because it has been held that the combustion of a paraffin hydrocarbon first occurs through a cracking or dehydrogenation process into hydrogen and an olefine hydrocarbon.[8]

In the case of ethane according to this view the first step of combustion is its transition to ethylene and hydrogen, but it has been

Fig. III., 4.—The rate of oxidation of ethylene in the presence of (a) copper, (b) lead and lead tetra ethyl (Δ), compared with ethylene alone.

shown that the oxidation characteristics of ethylene are decidedly different from those of ethane. Gardner [9] found that the thermal decomposition of ethane occurs only very slowly at 550°, whilst it can be shown that oxidation begins at 490° and even lower.
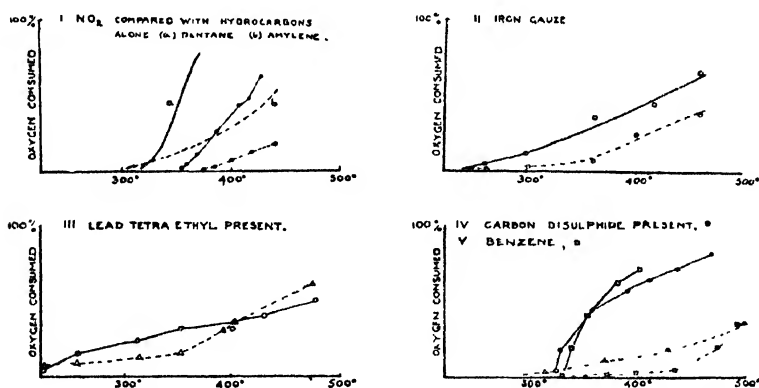
Fig. III., 5.—The action of inhibitors on the oxidation of pentane and amylene at different temperatures.

Bone and Stockings [6] in their researches on ethane found only small amounts (of the order 1 per cent.) of ethylene in the products of combustion of ethane in oxygen, and in the light of recent researches this small amount

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[8] Lewis, *J.C.S.*, 1555, 1927. [9] *Fuel*, **4**, 430, 1925.

can be as well attributed to autoxidation, according to the following equation, as to

$$F(O_2) + C_2H_6 \rightarrow FO + C_2H_4 + H_2O$$
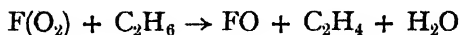
thermal decomposition.

A comparative study of the action of various inhibitors on the slow combustion of *n*-pentane and amylene respectively showed that amylene is usually much more sensitive to the action of inhibitors than pentane. Thus, hydrochloric acid gas reduced the rate of oxidation of amylene at 210° by three fold, but was without any marked effect when pentane was undergoing combustion. Another interesting distinction was indicated when pentane was found to be more effective than amylene in inhibiting the combustion of carbon disulphide in air.

A selection of results obtained by the tube method, illustrating the difference in effect of various inhibitors on the oxidation rate at different temperatures of amylene and pentane respectively in air is given in Fig. 5.

When benzene vapour was used as an inhibitor a far greater yield of phenol was obtained with the pentane-air mixture than with the amylene mixtures undergoing slow combusion; this would seem to indicate the higher yield of accumulated peroxides in the case of the paraffin hydrocarbon.

The Mechanism of Combustion.

It would appear from these results that the hypothesis which postulates the primary formation of an olefine hydrocarbon from a paraffin hydrocarbon as a first step in combustion is inadequate, because the olefine hydrocarbon has markedly different oxidation characteristics from the parent paraffin hydrocarbon. The olefine hydrocarbon has anti-knock properties whereas the paraffin hydrocarbons are prone to knock in an engine. Berl and colleagues suggest that the primarily produced olefine is in a "nascent" state so the oxidation characteristics would presumably be different from the ordinary hydrocarbons.[10] The conversion of a paraffin hydrocarbon into an alcohol as a first step during combustion according to the Armstrong-Bone hydroxylation theory, appears to be also incorrect since alcohols possess high anti-knock action. Similarly, Edgar's hypothesis that aldehydes are the primary oxidation products of paraffin hydrocarbons appears to be inadequate in the light of engine experiments which show that aldehydes do not cause detonation in the engine.[2] It will be shown later that the temperature coefficient of oxidation of alcohols and the corresponding aldehydes is smaller than the corresponding paraffin hydrocarbons with the possible exception of methane. These results are in agreement with the findings of Tizard and Pye,[11] that fuel vapours possessing low temperature coefficients of oxidation possess anti-knock action.

Objections have been raised against the hydroxylation theory on the ground that alcohols are oxidised only with difficulty. Layng and Youker[7] studied the oxidation characteristics of heptane and heptyl alcohol and concluded that the oxidation of heptane in the gas phase is not through its normal alcohol.

Stephens[12] also concluded from his researches on the oxidation of alcohols and hydrocarbons that the oxidation of saturated hydrocarbons does not go through the alcohol stage. When acetic anhydride vapour

[10] *Z. physik. chem.*, **139**, 453, 1928. [11] *Phil. Mag.*, **79**, 1922; 1094, 1926.
[12] *J. Am. Chem. Soc.*, **50**, 2523, 1928.

was introduced into the reaction tube no esters were formed. He found that the main products obtained from alcohols were liquids of high boiling-point, presumably ethers.

Bone and Stockings[6] did not find ethyl alcohol in the products of combustion of ethane although according to their hypothesis, ethyl alcohol is the first transition of ethane.

$$C_2H_6 \rightarrow C_2H_5OH.$$

They concluded that the alcohol was oxidised to aldehydes, etc., as soon as formed on account of its ease of oxidation, but it will be shown later that alcohols are not readily oxidisable in air during small times of heating so any conversion of ethane into ethyl alcohol by primary hydroxylation during rapid heating could result in appreciable quantities of ethyl alcohol being present in the products of combustion. None was found in the combustion products of several grams of ethane, although when alcohol was added to the ethane-air mixtures sufficient alcohol remained unchanged in the reaction products to be detected.
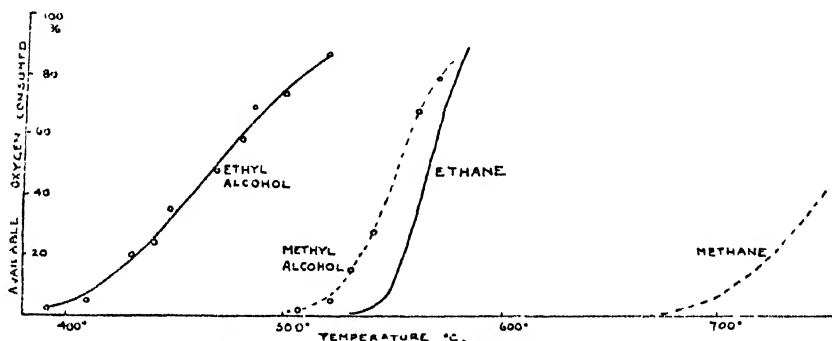
FIG. III., 6.—The rate of oxidation of (a) ethane and ethyl alcohol, (b) methane and methyl alcohol at different temperatures.

Comparative experiments were carried out with ethane and ethyl alcohol and very marked differences were recorded, especially with the yield of aldehydes. Using a 10·4 per cent. ethyl alcohol air-mixture it was found that by the tube method at 440° only a small yield of aldehydes (less than 2 per cent. of the alcohol used) was obtained. At 575° the yield was 4·5 per cent., whilst some unchanged alcohol could be detected in the exit gases. Even at 650° some alcohol remained unchanged in the mixture. Ethane at 575° underwent considerable oxidation producing a profusion of aldehydes, etc., but no alcohol could be detected in the products of combustion of five grams of ethane (mixture strength about 17 per cent.). The addition of alcohol (8 per cent.) to the ethane mixture before passing through the hot tube resulted in the presence of some alcohol in the exit gases.

The rate of oxidation of ethyl alcohol and methyl alcohol at various temperatures was determined by measuring the depletion of oxygen in the gas mixture after 20 seconds' heating in its passage through a hot tube. The results are shown in Fig. 6 from which it will be seen that ethyl alcohol is a much more slowly oxidisable substance than ethane, the temperature coefficient being about a third of that of ethane.

Methyl alcohol also has a low temperature coefficient of gaseous oxidation but less so than methane which is unique amongst the hydrocarbons in its resistance to oxidation.

Some quantitative results are given in Table I., for the slow oxidation of methyl, ethyl and isoamyl alcohol in air by the tube method, with and without "anti-knockers," the amounts of oxidation products being expressed as percentage quantities of the fuel weight used.

It will be observed that oxidation of the alcohols only occurs extensively at high temperature, *viz.* about 500° C., so it appears highly improbable that the aldehydes found in profusion as intermediate products in the combustion of hydrocarbons are produced from alcohols.

TABLE I.

(a) *The slow oxidation of methyl alcohol at 500°* :—

Mixture strength	.	22	9·8	8·5 (with iron carbonyl)
Aldehydes	.	14	9	1·2
Acids	.	0·4	0·6	1·3
CO_2	.	0·8	0·7	2·6
H_2	.	0·7	0·5	Nil
CO	.	3	5	—

(b) *The slow oxidation of isoamyl alcohol at 525°* :—

Mixture strength	.	3·9	7·7 (with iron carbonyl)	6 (with lead tetra ethyl)
Aldehydes	.	5	0·5	1·5
CO_2	.	1	1·5	1
CO	.	7	2	6

(c) *The combustion of ethyl alcohol at 575°* :—

Mixture strength	.	10·4
Acids	.	0·8
Aldehydes	.	4·5
Hydrogen	.	2
CO_2	.	6 per cent.
CO	.	Small quantity.

(d) *The combustion of ethyl alcohol at 675°* :—

Mixture strength	.	13·7	8·1	3·6
CO_2	.	25	27	33
CO	.	1	1	1
H_2	.	1·5	1	1

(e) *The combustion of ethyl alcohol at 725°* :—

Mixture strength	.	12 *	21 (with iron carbonyl)	20·5 (with lead tetra ethyl)
CO_2	.	31	25	23
CO	.	2	1	2
Acids	.	0·4	1	0·6
Aldehydes	.	0·5	1·7	1·8
Water	.	7·5	8·0	7·8

* This mixture occasionally flashed with a blue flame.

It is interesting to note that lead tetra ethyl in some instances with ethyl alcohol mixtures was found not to decrease the aldehyde yield appreciably but occasionally to increase it. With a 22 per cent. alcohol mixture a small quantity of lead tetra ethyl at 500° nearly doubled both the aldehyde and carbon dioxide yield. It would thus appear that the inhibitory action of lead tetra ethyl on aldehyde formation in the slow combustion of hydrocarbons must be due to the inhibition of a parent substance other than alcohol postulated by the hydroxylation theory.

The view that aldehydes are the result of the decomposition and inter-action of organic peroxides has been strikingly confirmed by recent re-searches on the gumming of olefine hydrocarbons.[13]

The finding of alcohols amongst the oxidation products of hydrocarbons does not necessarily support the view that these precede the aldehyde formation ; alcohols might be formed from secondary reactions. This is discussed later.

The Formation of Alcohols and Glycols during the Combustion of Hydrocarbons.

Although ethyl alcohol has not been isolated from the products of combustion of hydrocarbon vapours in air or oxygen, hydroxyl compounds, presumably glycols, appeared to be present in small quantities in the condensed products of combustion. About 30 c.c. of hexane were passed in the form of vapour with air through a hot glass tube at 500° C., and the combustion products were condensed in a U tube immersed in a freezing mixture at − 80° C.

The distillate to 100° from the condensed products gave no indication of either methyl or ethyl alcohol, and no evidence was obtained of their presence in the distillate by Verley and Bolsing's method of acetylation.[14] Using this same method of acetylation, it was found that the condensate after standing in a vacuum desiccator showed the presence of very small amounts of organic hydroxyl compounds. It is possible that glycols could be formed during combustion by the action of steam on alkylene oxides and not necessarily by any process of primary hydroxylation.

The oxidation of molten paraffin wax by a stream of air or oxygen results in a large variety of oxidation products, including alcohols, esters, aldehydes, ketones, acids, etc. Bone has recently drawn attention to the findings of Landa on the oxidation of paraffin wax,[15] m.p. 51° C. Methyl, ethyl and higher alcohols were found in the oxidation products in addition to aldehydes, acetone, methyl ethyl ketone, etc., and their presence is regarded as sufficient evidence to justify the hydroxylation hypothesis.[16]

Kelber[17] and Grun[15] had previously studied the oxidation of paraffin wax and though they identified alcohols amongst the oxidation products they considered that the peroxidation mechanism of combustion explained satisfactorily the results obtained.

The formation of alcohols could occur in several ways other than by primary hydroxylation. Autoxidation or by intramolecular decomposition of a dimoloxide as suggested by Stephens[12] could result in alcohols, e.g. according to the following equations :—

$$CH_4(O_2) + CH_4 \rightarrow 2CH_3OH \qquad (I)$$
$$CH_4(O_2) + CH_4 \rightarrow CH_4(O_2)CH_4 \rightarrow 2CH_3OH \qquad (II)$$

Rieche and co-workers[18] have shown that alcohols result from the decomposition of alkyl hydrogen peroxides and dialkyl peroxides.

These peroxides are formed primarily from ethane during slow com-bustion according to the Callendar and Mardles' hypothesis as follows ; and so the formation of alcohols can be accounted for in this manner :—

$$C_2H_6 + O_2 \nearrow CH_3OOCH_3 \rightarrow CH_3OH + HCHO$$
$$\searrow C_2H_5OOH \rightarrow C_2H_5OH, \text{ etc.}$$
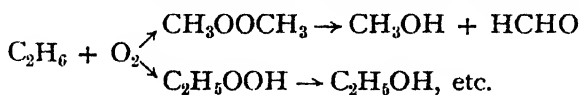
[13] " Symposium on Gumming," *J. Inst. Pet. Tech.*, **77**, 645, 1929.
[14] *Ber.*, **34**, 3354, 1901.   [15] *C.R.*, **186**, 589, 1928.   [16] *Nature*, **122**, 203, 1928.
[17] *Ber.*, **53**, 13, 1567, 1920.   [18] *Ber.*, **62**, 2460, 1929.

The researches of Gelissen and Hermans,[19] and others, on the reaction of organic peroxides show that esters are formed by autoxidation of hydrocarbon molecules. Brodie (1864) showed that phenyl benzoate resulted as one of the decomposition products of dibenzoyl peroxides. Gelissen and Hermans found phenyl benzoate in the products of interaction of dibenzoyl peroxide and benzene, the course of reaction being as follows :—

Main reaction (by reaction)

$$C_6H_5COOH + RC_6H_5 + CO_2 \qquad C_6H_5COOR + HC_6H_5 + CO_2$$
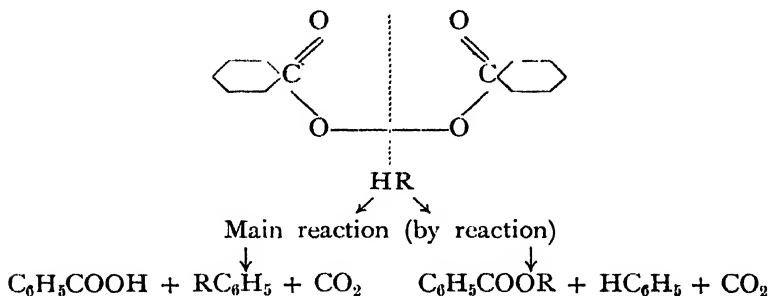
Blair and others [20] noted the probable presence of hexyl hexoate in the products obtained by the action of ozone on boiling hexane.

Alcohols therefore could also result from the hydrolysis of esters produced by the interaction of peroxides with fuel molecules.

Pease [21] considers that the formation of alcohols is possibly due to the tendency of hydrocarbons to undergo demethanation, the formations occurring as follows :—

$$C_3H_8 + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + CH_3OH.$$
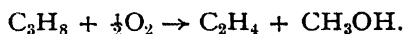
It has also been suggested that alcohols are formed from aldehydes by Cannizzaro's reaction.

The Hydroxylation and Peroxidation Theories of Combustion of Hydrocarbons.

Acetaldehyde is one of the intermediate products of combustion of ethylene and its presence in the condensate of combustion products is regarded by Bone as a proof of the validity of the hydroxylation hypothesis. He assumes acetaldehyde is produced through vinyl alcohol, the monohydroxy derivative of ethylene [22] as follows :—

$$\begin{array}{ccccc} CH_2 & & CH_2 & & CH_3 \\ \| & \longrightarrow & \| & \longrightarrow & | \\ CH_2 & & CHOH & & CHO \end{array}$$

There is an important alternative to this method of formation of acetaldehyde based on the peroxide theory of combustion.

According to the Prileschajew reaction [23] alkylene oxides are formed by interaction of a peroxide and an olefine. Thus, by simple autoxidation of ethylene, ethylene oxide can be produced and this oxide by direct decomposition yields acetaldehyde.

[19] *Ber.*, 285, 1925.
[21] *J. Amer. Chem. Soc.*, 1839, 1929.
[23] *Ber.*, 42, 4811, 1909.

[20] *J. Soc. Chem. Ind.*, 43, 289, 1924.
[22] *Nature*, 122, 203, 1928.

$$CH_2 \atop \underset{CH_2}{|} + (O_2)R \longrightarrow {CH_2 \atop \underset{CH_2}{|}}\!\!\!\!>\!O + RO$$

$${CH_2 \atop \underset{CH_2}{|}}\!\!\!\!>\!O \longrightarrow {CH_3 \atop \underset{CHO}{|}}$$
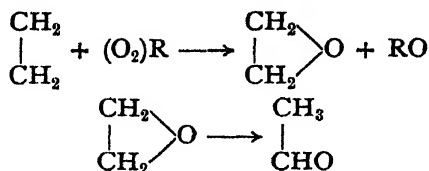
The experiment was tried of passing ethylene oxide vapour mixed with air (30 per cent. mixture strength) through a glass tube gradually heated. Just below 200° aldehydes, carbon dioxide and water were detected. Acetaldehyde in relatively large quantities was identified amongst the products of reaction.

Imatiew and Leontowitch [24] have shown that in the presence of alumina ethylene oxide is transformed into acetaldehyde whilst the higher alkylene oxides form both isomeric aldehydes and ketones.

Peroxides in the products of combustion of ethylene and ethane were found and inhibitors such as aniline, lead tetra ethyl inhibited their formation. Autoxidation of the aniline vapour to gumming products occurred and it was found that corresponding to the decrease in "active" oxygen a decreased aldehyde yield was obtained. Thompson and Hinshelwood [25] in a study of the oxidation of ethylene have shown that surfaces have a marked action on the rate of oxidation. They consider that the mechanism of combustion is primarily through peroxidation and suggest that hydroxylation occurs by subsequent interaction of peroxide and hydrocarbon.

The Oxidation of Aldehydes.

Results of oxidation experiments with acetaldehyde and n. valeraldehyde are shown in Fig. 7a ; the amount of oxygen depletion after the aldehyde-air mixtures of approximately 22 per cent. and 17 per cent. mixture strength respectively had passed through a hot glass tube with time of heating of about 20 seconds was less than the corresponding paraffin hydrocarbon.
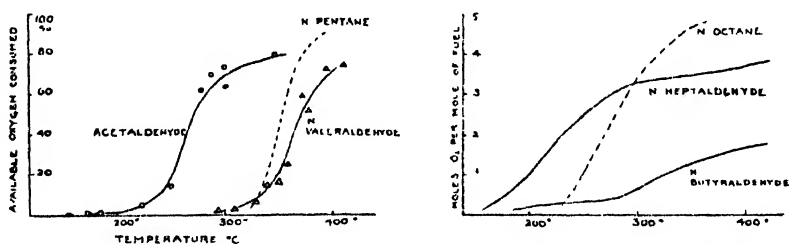
FIG. III., 7.—The rate of oxidation of (a) acetaldehyde, and N. valeraldehyde, (b) Heptaldehyde and N. butyraldehyde (Pope, Dykstra, and Edgar).

The curves shown for the aldehydes are also less steep than those for the paraffin hydrocarbon indicating a lower temperature coefficient of gaseous reaction. These findings are in keeping with the engine results that aldehydes do not cause detonation in the engine.

The oxidation of n. butyraldehyde and n. heptaldehyde has been carefully studied by Pope, Dykstra, and Edgar [26] in connection with an investigation

[24] Ber., 36, 2016, 1903.   [25] Proc. Roy. Soc., A. 125, 27, 1929.
[26] J. Amer. Chem. Soc., 51, 1875, 2203, 2213, 1929.

on the rates of oxidation of octanes in air by the tube method. A selection of their results dealing with the oxygen consumption in terms of O_2 mols. per mol. of fuel is shown in Fig. 7b. It will be seen that the aldehydes show a much lower temperature coefficient of oxidation than the hydrocarbon.

The oxidation characteristics of the aldehydes are different from those of the paraffins: thus, ethyl alcohol and lead tetra ethyl have a decided effect on the glow and oxidation of hydrocarbons but only a small or moderate effect on the aldehydes.[5]

These findings taken in conjunction with the fact that aldehydes and alcohols do not cause detonation in an engine confirm the conclusion of Callendar that the intermediate products of combustion, viz., aldehydes, acids, ketones, etc., are not responsible for detonation but a prior compound which yields these substances. Inhibitors act not by destroying aldehydes after they were formed but by preventing their formation. That is to say the dopes must take effect directly on the primary compound, viz., a peroxide.

The Oxidation of Isomeric Hydrocarbons.

The work of Edgar and colleagues has shown that marked differences in the oxidation of isomeric octanes can occur. Generally, the long chain normal hydrocarbon is far more susceptible to oxidation than one with several branches; thus, normal octane begins to oxidise at just above 200° whilst 2.2.4 trimethyl pentane does not begin to oxidise until 500° is reached, Fig. 8b. Whilst normal octane causes violent knocking in an
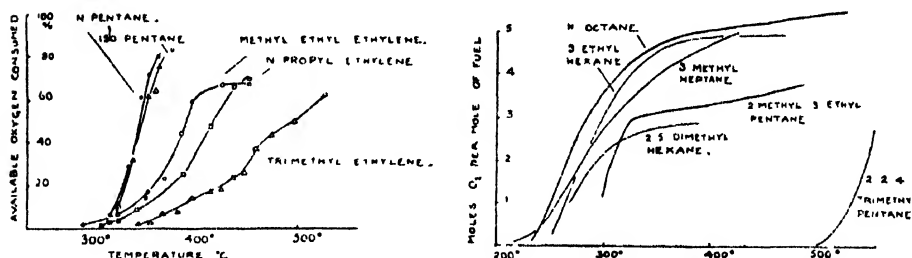
Fig. III., 8.—(a) The oxidation rate at different temperatures of isomeric pentanes and amylenes. (b) The oxidation rate of isomeric octanes (Pope, Dykstra, and Edgar).

engine the isomeric variety of more compact molecular form resembles benzene in its anti-knock action. It has been already pointed out that the temperature coefficient of oxidation of the stable octane is considerably less than normal hexane.[27]

A similar behaviour was found with the amylenes and to some extent with the pentanes (Fig. 8a); the curve for normal propyl ethylene is considerably more steep than that for tri-methyl-ethylene.

Summary.

1. The paraffin hydrocarbons of the normal series (apart from methane) possess a relatively high temperature coefficient of gaseous oxidation, and in this and other respects differ from the olefine hydrocarbons, alcohols, and aldehydes.

From this standpoint alone it appears improbable that the first transformations of paraffin hydrocarbons during combustion are to (a) alcohols (Bone-Armstrong); (b) to olefines (Kelber, Lewis, Berl, etc.); (c) to aldehydes (Pope, Dykstra, and Edgar).

[27] R. & M., No. 1374 (Air Ministry.)

The oxidation results are best explained by the peroxidation theory of combustion.

2. Inhibitors and surfaces, especially those of metals, reduced the temperature coefficient of gaseous reaction and raised the self-ignition temperature.

The action of lead and iron was similar to lead tetra ethyl and iron carbonyl respectively.

3. The action of inhibitors varied considerably with the class of fuel vapours. The olefine hydrocarbons were more sensitive than the normal paraffin hydrocarbons to the action of inhibitors.

During the combustion of pentane there was a greater accumulation of peroxides than with amylene.

4. Results obtained with the oxidation of isomeric hydrocarbons show that the normal varieties are far more susceptible to oxidation than those with several branches, also the temperature coefficient of gaseous reaction of the normal hydrocarbons was higher corresponding to greater detonation tendencies.

IV. THE OXIDATION OF FUEL VAPOURS IN AIR; EXPERIMENTS WITH (a) AROMATIC HYDROCARBONS, (b) CYCLOHEXANE AND (c) CYCLOHEXENE.

It has been an early experience that the aromatic hydrocarbons, benzene, toluene, xylenes, etc., do not cause detonation in an engine until compression ratios above seven are reached, and more recently it has been shown that cyclohexane (hexahydrobenzene) and cyclohexene (tetrahydrobenzene) possess similar anti-knock properties. Nash and Howes[1] have given the following values (Table I.) for the relative anti-knock properties of these hydrocarbons when added to a straight-run petrol :—

TABLE I.

20 per cent. cyclohexane,	equivalent to	1	c.c. ethyl fluid per gallon.					
,, ,,	cyclohexene	,,	,, 2·4	c.c.	,,	,,	,,	,,
,, ,,	benzene	,,	,, 2·1	c.c.	,,	,,	,,	,,
,, ,,	toluene	,,	,, 2·75	c.c.	,,	,,	,,	,,

Callendar[2] found that with additions of 5 per cent. volume to a straight-run petrol, benzene raised the H.U.C. ratio by 1 per cent., toluene by 2 per cent., and o-xylene by 0·6 per cent.

In order of anti-knock properties the hydrocarbons are, therefore, toluene, cyclohexene, benzene, xylenes, cyclohexane, hexane.

No satisfactory explanation has been put forward to account for the anti-knock properties of the aromatic hydrocarbons and their derivatives, or why cyclohexane behaves so differently with regard to engine detonation from the corresponding straight chain hexane. It is true that the aromatic hydrocarbons possess high self-ignition temperatures, as seen in Table II., but the self-ignition temperature of cyclohexane is not much different from that of n. hexane of low anti-knock value ; many investigators have shown that the self-ignition temperature cannot be regarded as a criterion of anti-knock properties.

The temperatures of initial combustion of the fuel vapours in air, determined by the tube method with 20 seconds' heating and noting the first appearance of aldehydes, etc., were highest with benzene, viz., 693° for 2·9 per cent. mixture strength, 682° for 4·3 per cent., and 670° for 18·5 per cent. With toluene the temperatures were considerably lower and with meta-xylene lower still, as appears from Table III.

[1] *Nature*, Feb. 23rd, 1929.   [2] *Aeronautical R. and M.*, 1013.

Some difficulty was experienced in the investigation with the aromatic hydrocarbons because the mixtures were liable to self-ignite when oxidation began to proceed with any degree of vigour; in the reaction tube a 12 per cent. benzene vapour mixture in air inflamed at 715°. The vapour of toluene and xylene could sometimes be passed slowly through a horizontal glass tube heated to 700° without inflammation occurring if a fairly rich mixture was employed. When the fuels were sprayed into the tube, however, *m.* xylene caught fire at 610° and cymene (methyl isopropyl benzene, b.p. 174-176°) at 571°.

Although cymene and cumene (isopropyl benzene) were found to possess relatively high self-ignition temperatures, yet it has been shown by Callendar[2] that a 5 per cent. addition of cumene to a "straight-run" petrol lowered the H.U.C. ratio by 0·4 per cent.

With regard to the anti-knock action of aromatic hydrocarbons from the standpoint of the chain reaction hypothesis it has been stated by Hinshel-

TABLE II.

Compound.	Tauss and Schultz.[3]	Tizard.[4]	Masson and Hamilton.[5]	Berl and Others.[6]
Benzene	730	419	656	588
Toluene	810	422	633	624
Xylene	750	—	618	514
Cyclohexene . . .	—	—	—	378
Cyclohexane . . .	—	387	—	400
n. Hexane . . .	487	366	520	388

TABLE III.

(a) *With toluene.*

Mixture strength . .	6 per cent.	13·8 per cent.	26 per cent.
T.I.C.	543°	527°	522°

b) *With m. xylene.*

Mixture strength . .	4·8 per cent.	8 per cent.	9·8 per cent.
T.I.C.	523°	518°	513°

wood that in the oxidation of benzene vapour chains play a part, though not so important a part as for example in the combination of hydrogen and oxygen, whilst according to the peroxide theory of combustion and detonation it is presumed that during the slow combustion of the vapour of the aromatic hydrocarbons there is little or no accumulation of explosive peroxides. It is of interest to note, in connection with the peroxide theory, that though cyclohexene when freshly prepared has a high anti-knock value, yet after storage, when cyclohexene peroxides have formed in small amounts, the fuel becomes pro-knock in action.

The experimental work has been carried out with the object of determining the oxidation characteristics of the aromatic hydrocarbons, especially with regard to the temperature coefficient of gaseous reaction and with regard to the action of inhibitors. The main results obtained have confirmed the findings of previous investigations, *viz.*, that the higher the anti-knock value the lower is the temperature coefficient of gaseous reaction. The action of inhibitors has been invariably that of decreasing the temperature coefficient. These findings are in accord with the peroxide theory of

[3] *Z. angew. Chem.*, **40**, 247, 1927.   [4] *Motor Wagen*, **28**, 682, 1925.
[5] *Ind. Eng. Chem.*, **19**, 1355, 1927.   [6] *Z. physik. Chem.*, **139** (Haber-Band) 453, 1928.

combustion, the rate of reaction being considered as a function of the concentration of activated peroxides and not of the proportion of fuel and oxygen molecules according to the law of Guldberg and Waage.

Experimental.

The experimental work involved the use of two methods, which in brief are (a) the closed bulb method, by which the gas mixture was maintained at constant temperature in a hard glass bulb, and the course of the reaction followed by pressure change, and (b) the heated tube method by which the gas mixture was passed through a glass tube heated in an electric furnace and the products of combustion examined; the time of heating was kept at approximately 20 seconds. A full description of the apparatus and methods has been given elsewhere.[7]

A measure of the oxidation rate in a gaseous mixture is determinable by ascertaining the proportion of oxygen consumed in the mixture during any arbitrary period of time and the temperature coefficient of gaseous reaction is indicated by the steepness of the curves relating the temperature and proportion of oxygen consumed. Such curves obtained with 20 seconds' heating for benzene, toluene, m. xylene, cyclohexene and cyclohexane are shown together in Fig. 1 (the mixture strengths are approximately 12 per cent.).
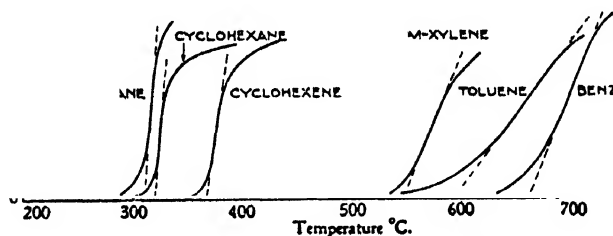
FIG. IV., 1.—The rate of oxidation in air of the vapour of benzene, toluene, cyclohexane, etc., at different temperatures. (The slope of curve indicates temperature coefficient of gaseous reaction.)

It will be seen that for toluene of highest anti-knock value the curve is decidedly less steep than that of either m. xylene or benzene.

The steep curve of normal hexane is included for purpose of comparison. The curves for cyclohexane and cyclohexene are of special interest. It appears that though the curve is relatively steep yet it is shorter, even at high temperatures a small proportion of oxygen remaining. It is probable that with these hydroaromatic compounds an inhibitor is produced amongst the products of combustion. Presumably this is phenol or its derivatives for relatively large quantities of phenolic bodies have been isolated from the products of combustion of these substances. A similar behaviour was found with the aldehydes, the inhibitor in this case being presumably carbon monoxide produced by the thermal decomposition of the aldehydes. The combustion of carbon disulphide is another instance of a fuel supplying its own inhibitors.

The lower rate of gaseous reaction with the hydrocarbons of higher anti-knock value can be demonstrated by the bulb method, the rate of

pressure change under isothermal conditions being least with toluene. Results of experiments by this method are shown in Figs. 2 and 3.

With toluene vapour in air (about 12 per cent.) at 485°, a steady absorption of oxygen occurred with slight fall in pressure and development of pungent fumes which appeared as a fog in the cool portion of the tube. After about 80 minutes the pressure rose relatively sharply. At 500° the changes were quicker and at 520° no fall in pressure was observed.

With *meta* xylene a similar behaviour was found but the pressure changes were much more rapid and occurred at lower temperatures.
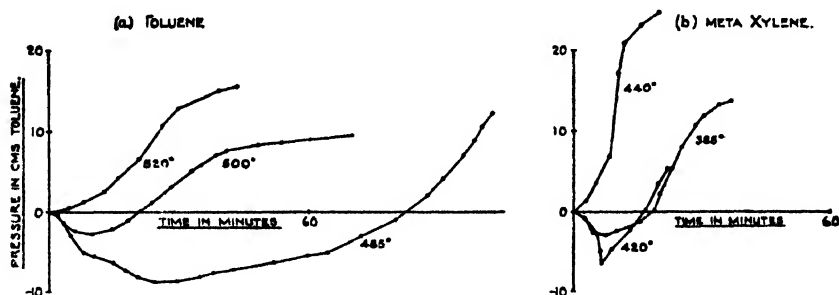
Fig. IV., 2.—Pressure changes during the oxidation in air of the vapour, of (a) toluene, (b) meta-xylene under isothermal conditions.
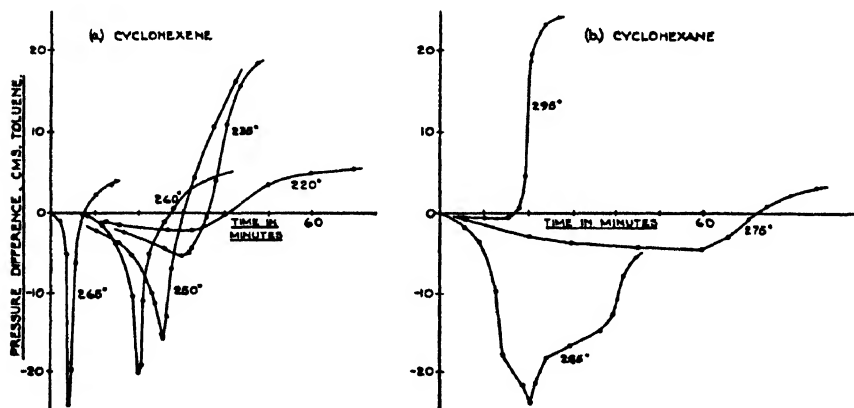
Fig. IV., 3.—Pressure changes during the oxidation in air of the vapour of (a) cyclohexene and (b) cyclohexane under isothermal conditions.

Analyses of the contents of the bulbs after the completion of the experiment showed that a small percentage of the oxygen usually remained. At lower temperatures when the pressure changes were small and very slow a large proportion of the oxygen remained although it appeared from the cessation of differences in pressure that the reaction was complete after two or three hours' heating.

With cyclohexene and with cyclohexane at lower temperatures the gaseous reaction was associated with first a considerable fall in pressure and then with a relatively sudden rise.

The behaviour of cyclohexane resembled hexane to some extent; thus, at 295° cyclohexane vapour absorbed oxygen, there being at first little or no pressure change, then suddenly the pressure rose.

With cyclohexene no marked induction period was observed, and the pressure change did not appear to be so rapid as with cyclohexane.

The Action of Inhibitors and Metal Surfaces.

The action of inhibitors such as phenol, aniline, etc., on the slow combustion of benzene and toluene cannot be tested satisfactorily because the inhibitor itself is oxidised by the air at the higher temperatures.   Some
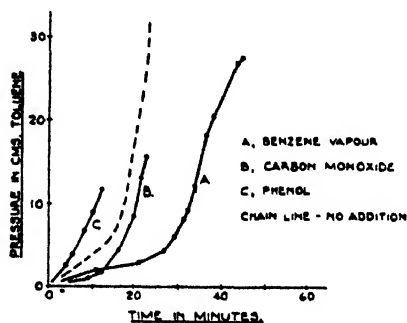
Fig. IV., 4.—The influence of benzene vapour carbon monoxide and phenol on the oxidation in air of cyclohexane vapour (bulb experiments).
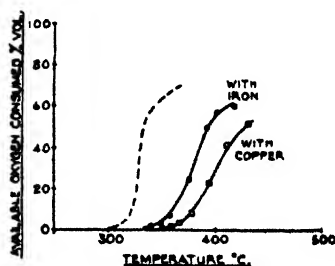
Fig. IV., 5.—The influence of (a) iron and (b) copper on the oxidation in air of cyclohexane vapour (tube experiments).

experiments were carried out with phenol vapour on the aromatic hydrocarbons but no marked effect was found. With cyclohexane, however, when a little benzene vapour was added to the mixture in the bulb a definite inhibitory effect was observed.

Similar results were obtained with carbon monoxide and coal gas, only to a lesser degree. Phenol when tried was found to undergo oxidation itself at 300°.

The results obtained are shown in Fig. 4.

Both benzene and phenol were tried as inhibitors in the case of cyclohexane by the tube method. Phenol vapour was found to be more effective than benzene vapour in inhibiting although the effect in either case was not great. The effect of the inhibitor, present in an amount approximately 10 per cent. of the fuel vapour, was to raise the temperature corresponding to the steep portion of the curve by about 20° in the case of phenol and 12° in the case of benzene.
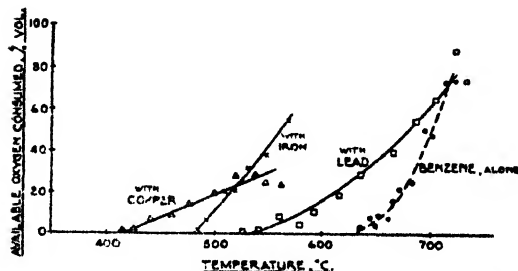
Fig. IV., 6.—The influence of (a) copper, (b) iron, and (c) lead on the oxidation in air of benzene.

Metal surfaces were found to be far more effective than the organic inhibitors ; thus both iron and copper gauze when introduced into the reaction tube raised the temperature of reaction about 50° and modified considerably the temperature coefficient, copper being more effective than iron.

Results with iron and copper surfaces on the slow combustion of cyclohexane by the tube method are shown in Fig. 5.

Experiments were carried out to determine the influence of iron, copper and lead on the slow combustion of benzene. The metals lowered the temperature when oxidation began, by over 200° in the case of copper, and considerably affected the temperature coefficient of gaseous reaction, copper being more effective than lead and lead more than iron in this respect.

The results are shown in Fig. 6.

Products of Slow Combustion.

The products of slow combustion of the aromatic hydrocarbons were not dissimilar from those of the paraffin and olefine hydrocarbons, aldehydes, acids, water, carbon monoxide and carbon dioxide being present.

Diphenyl and phenol were present in the combustion products of benzene. A considerable amount of tar and carbonaceous matter was formed and small amounts of peroxide compounds were detected.

The metals were found to raise the self-ignition temperature, to lower the temperature of initial oxidation and to decrease the amount of aldehydes and acids whilst increasing the yield of carbon dioxide. This behaviour was found to be general with all the fuel vapours examined.

Copper, brass and bronze were found to be more effective than lead and iron, which were more active than zinc or aluminium.

Quantitative analyses were made of the gases produced during the oxidation of the aromatic hydrocarbons with and without the vapours of iron carbonyl and lead tetra ethyl. It was found that these metallic dopes behaved similarly to the corresponding metal. At 700° the amount of reaction of a 12·4 per cent. benzene mixture in the glass tube was increased when a small amount of iron carbonyl vapour was added. Similarly with a toluene mixture it was found that the oxidation was more advanced at 700° in the presence of either lead tetra-ethyl or iron carbonyl vapour.

A series of experiments has been carried out by Berl, Heise, and Winnacker,[6] dealing with the action of iron carbonyl and lead tetra-ethyl on the combustion of hexane and cyclohexane in oxygen. They have reported that both cyclohexane and hexane vapour at 400° in oxygen is less oxidisable in the presence of small amounts of lead tetra-ethyl.

The behaviour of the metal surfaces, as shown in Fig. 5 is to inhibit the combustion in air of cyclohexane vapour, yet from Fig. 6 it will be found that with benzene vapour the metals lower the temperatures of oxidation and increase the rate of the gaseous reaction.

This interesting behaviour of surface catalysts and inhibition has not been explained, but it is important to note that in the presence of metals the amount of peroxide compounds detectible in the gas mixture is reduced to a minimum and the glow of chemical change occurs intensely at the surface of the metal. The conclusion that metals formed from anti-knockers act by reducing peroxides or preventing their formation before intramolecular oxidation occurs[7] has been confirmed by Berl, Heise, and Winnacker.

Conclusions.

1. The vapours of the aromatic hydrocarbons did not oxidise in air readily below 500° C., benzene being the most resistant and requiring a temperature of 700° C. before vigorous reaction began in the glass tube. Toluene oxidised appreciably at about 650° and xylene at about 575°. The temperature

[7] Callendar and others, 1927.

·coefficient of gaseous reaction was least with toluene which possessed the highest anti-knock value.

2. Cyclohexane vapours in air oxidised appreciably at about 315°, being similar to hexane in this respect, and cyclohexene became oxidised at about 375°. The temperature coefficient of gaseous reaction.was less with cyclohexene than with either cyclohexane or hexane.

Small amounts of phenol were detected in the combustion products of the hyroaromatic hydrocarbons and the phenol apparently tends to inhibit the combustion in the latter stages.

3. The action of inhibitors and metal surfaces was to decrease the temperature coefficient of gaseous reaction and to inhibit the formation of peroxide compounds ; the self-ignition temperature was raised and the temperatures of oxidation were raised with cyclohexane and lowered in the case of benzene when metals were present.

4. The results of oxidation are in accord with the peroxide theory of combustion.

V. THE OXIDATION OF ACETYLENE IN AIR.

The slow combustion of acetylene in air begins at temperatures as low as 200° in a glass vessel although the rate of oxidation only becomes appreciable at temperatures approaching 300°.

Peroxidation occurs to a considerable extent during the gaseous reaction and the final products of oxidation consist mainly of formaldehyde, formic acid, steam, carbon monoxide, carbon dioxide, etc. A little tar, but no free carbon, was obtained unless self-ignition occurred. Small amounts of hydrogen and ethane were found in the oxidation products but no benzene, due to polymerisation, was traced.

The oxidation of acetylene in air presents an interesting problem with regard to the sequence of reactions leading to formaldehyde, etc. The Armstrong-Bone hydroxylation hypothesis does not account for peroxidation or autocatalysis which occurs during combustion. Peroxidation could occur by the attachment of oxygen to the C . C bond or by entry between the C and H of the CH group. Formaldehyde and carbon monoxide would presumably result from the decomposition of the primarily formed peroxide.

It was found that the gas reaction could be modified to a considerable extent by the action of small quantities of carbon monoxide, carbon disulphide, benzene, phenol, aniline, lead tetra ethyl, iron carbonyl and other inhibitors. The degree of peroxidation was decreased by the inhibitors which in turn were autoxidised ; thus, benzene was autoxidised to phenol.

The formation and accumulation of explosive peroxides would account for the pro-knock action of acetylene, but it was found that the slow combustion of acetylene differed from that of hexane by having a lower oxidation rate.

Undoubtedly the strongly endothermic character of acetylene taken in conjunction with its liability to explosive self-ignition, with molecular disruption, would contribute to its pro-knock character ; but in some respects its oxidation resembles that of ethylene because the temperature coefficient of oxidation is smaller than that of most pro-knock substances.

A contributory cause to the low temperature coefficient of oxidation is the presence of relatively large quantities of carbon monoxide in the reaction products which behaves as an inhibitor. Bone and Andrew found[1] in a

mixture of equal volumes of acetylene and oxygen after oxidation 58·05 per cent. of carbon monoxide. They also reported that the oxygen is initially incorporated with acetylene during oxidation giving rise to an unstable molecule which rapidly undergoes thermal decomposition into formaldehyde and carbon monoxide.

Experimental.

The experimental work involves the use of two methods, *viz :* (*a*) The closed bulb method by which the gas mixture was maintained at constant temperature in a hard glass bulb, and the course of the reaction followed by pressure change; and (*b*) the heated tube method by which the gas mixture was passed through a glass tube heated in an electric furnace and the products of combustion examined. The time of heating was kept at approximately 20 seconds.

A full description of the apparatus and methods has been given elsewhere.[2]

Temperature of Initial Combustion.

Oxidation changes could be detected in the acetylene-air mixture at temperatures as low as 200° over a period of an hour. There was a slight rise in pressure due to the multiplication of molecules but the oxygen content only slightly decreased. Even at higher temperatures the amount of oxygen consumed during an hour was small; thus, at 350° after an hour only about a third of the available oxygen was consumed in a mixture containing 20 per cent. vol. acetylene.

When the gas mixtures were passed through a heated glass tube with a time of heating of about 20 seconds, they showed signs of change just below 400′, formaldehyde, water, carbon monoxide, etc., being detected.

The temperature of initial combustion determined in this way varied with the mixture strength. Results obtained by varying the mixture strength are given in Table I., from which it will be seen that the leaner mixtures require a higher temperature before oxidation begins.

TABLE I.

Mixture Strength Acetylene Per Cent. Vol.	Temperature of Initial Combustion.
6·5	440°
20	405°
23	390°
24	399°
28	358°
46	340°
64	340°
66	330°
75	338°
85	342°
93	354°

Sometimes the self-ignition occurred a few degrees above the temperatures given in Table I.

Inhibitors such as carbon monoxide or benzene raised the temperature when oxidation began, whilst on the other hand metal surfaces lowered the

temperature; thus iron filings when present in the reaction tube reduced the T.I.C. from 330° to 285° and copper foil reduced it to 305°. Lead and nickel had similar effects.

The inhibitors and metal surfaces in all cases raised the self-ignition temperature and reduced the temperature coefficient of gaseous reaction. There was also a decrease in the amount of peroxidation and yield of
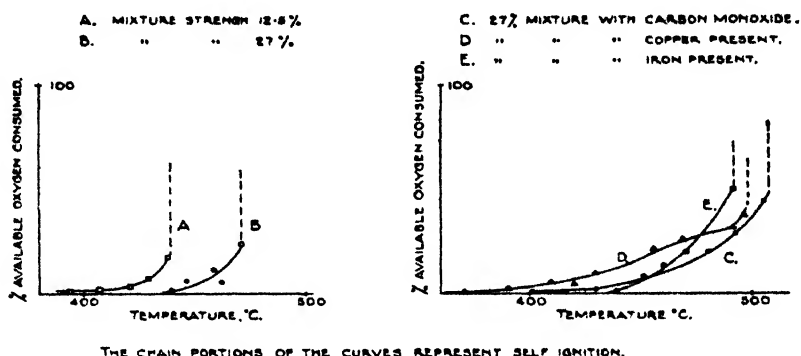
Fig. V., 1.—The oxidation of acetylene in air : rate of reaction at different temperatures. (Tube method.)

aldehydes. Aniline raised the self-ignition temperature of a 30 per cent. mixture to above 450°, and at 450° only a fifth of the available oxygen was consumed during its passage through the reaction tube.

Lead and copper foil did not have a strong influence in delaying spontaneous ignition, but the temperature when carbon dioxide was first observed was lowered by 10° with lead and 23° with copper ; a combustion carried out at 350° with a 20 per cent. acetylene-air mixture in the presence of iron turnings showed that 78 per cent. of the oxygen had been consumed and at 300°, 41 per cent. At 460° C., without metal present, only about half the acetylene was oxidised, approximately o·8 gr. of oxygen per gram of acetylene being consumed.

Some quantitative results of the analyses of different acetylene mixtures after oxidation in the tube, with and without dope and metal surfaces are shown in Fig. 1. It will be seen that increase in mixture strength tends to lower the temperature coefficient of gaseous reaction since though the temperature of initial combustion is lower the point when vigorous oxidation sets in is much higher. The complete curves could not be obtained, since self-ignition usually occurred when oxidation set in vigorously.

Fig. V., 2.—The oxidation of acetylene in air (15 per cent. mixture strength) at different temperatures; pressure changes with time (bulb method).

Oxidations at lower temperatures in glass bulbs, with and without dopes, could be conveniently followed by pressure changes using a toluene-filled gauge. Between 200° and 300° slight positive pressures were regis-

tered there being no marked induction period noticeable, whilst above 300° negative pressures were observed. Some results obtained are shown in Figs. 2 and 3, the latter giving the effect of inhibitors and metal surfaces. The curves obtained differ considerably from those of the paraffin hydrocarbons, there being no sudden development of pressure due to the decomposition of accumulated peroxides.

Metals accentuated the pressure changes whilst the inhibitors altered them according to whether their autoxidation resulted in a multiplication or decrease in the number of molecules. In the case of carbon disulphide as inhibitor the acetylene in turn inhibits the oxidation of the inhibitor, so delayed action is obtained.

The characteristic action of anti-knockers in delaying spontaneous ignition and controlling the rate of oxidation was especially noticeable when iron carbonyl or lead tetra ethyl was used.
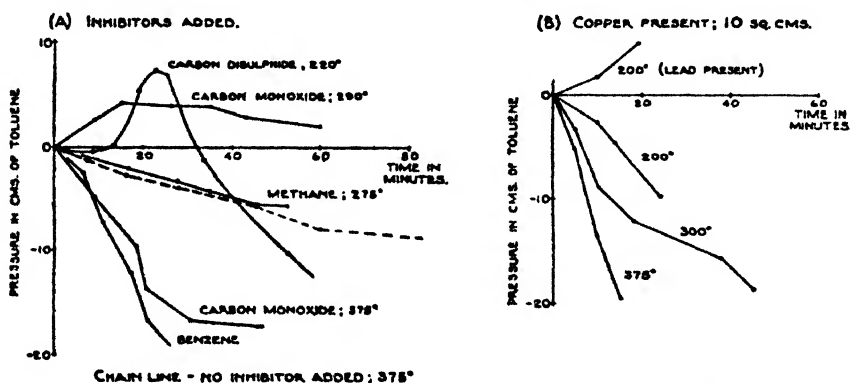
Fig. V., 3.—The oxidation of acetylene in air (15 per cent. mixture strength) with (A) addition of inhibitors, and (B) presence of metal surfaces.

A series of combustions was carried out using air which had passed across the surface of iron carbonyl.

At temperatures to 450°, oxidation during the passage of a 35 per cent. vol. acetylene-air mixture through the heated tube with a heating of 20 seconds was small and less than 10 per cent. of the available oxygen was consumed. Even at 520°, 65 per cent. of the oxygen in the mixture remained unconsumed.

With lead tetra ethyl vapour present in the proportion of about one part per thousand, the self-ignition temperature was raised 25°. An analysis of the reaction products from an oxidation at 365° showed that the amount of oxidation was practically the same as in the same mixture 30° lower, when no lead tetra ethyl was present.

Conclusions.

1. The results of the oxidation in air of acetylene at temperatures below the self-ignition temperature, with and without inhibitors, indicate that peroxidation occurs primarily.

Formaldehyde, formic acid, hydrogen, carbon monoxide, etc., are produced by the decomposition of the peroxides produced by the attachment of the oxygen molecule to the C.C. bond or by the inclusion between the carbon and hydrogen of the C.H. group.

2. Inhibitors and metal surfaces reduce the accumulation of peroxides and so affect the rate of gaseous reaction and reduce its temperature coefficient. The inhibitors are autoxidised in the process.

The decrease in amount of peroxidation is accompanied by smaller aldehyde yields.

ANODE PHENOMENA IN THE ELECTROLYSIS OF POTASSIUM ACETATE SOLUTIONS. PART II. DISCHARGE POTENTIAL OF THE ACETATE ION.

BY SOORYA N. SHUKLA AND OSWALD J. WALKER.

In 1898 Bose[1] found that the decomposition potential of a $3\cdot5$ N aqueous solution of potassium acetate between smooth platinum electrodes was $2\cdot05$ volts. Preuner and Ludlam[2] measured the potential difference at a platinum anode during the electrolysis of a $0\cdot5$ N solution of potassium acetate ($0\cdot5$ N also with respect to added acetic acid), and found a break in the current-potential curve not at $2\cdot05$ volts but at $2\cdot54$ volts. They also showed that at this potential ethane began to be evolved amongst the anodic gases, while the percentage of oxygen began to diminish. Fairweather and Walker[3] confirmed the existence of a definite potential for the formation of ethane in the electrolysis of a N solution of potassium acetate, but found the value to be about $2\cdot15$ volts. It has been generally assumed that Preuner and Ludlam's potential of $2\cdot54$ volts represents the " discharge potential " of the acetate ion at a smooth platinum electrode, though it has been pointed out by Gibson[4] that the evolution of ethane at this potential might also mean that at $2\cdot54$ volts the anode has acquired an oxidising potential high enough to allow the reaction to proceed. It is possible, however, to ascribe the evolution of oxygen below this potential to the primary discharge of acetanions followed by a secondary reaction of the discharged ions with water. For the present, therefore, we shall refer to this " discharge potential " as the " critical " potential for the formation of ethane, without making any assumptions as to its actual meaning.

Preuner and Ludlam's value, while it has been generally accepted as being correct, is much higher than that of other investigators, and makes the " discharge " potential of the acetate ion abnormally high in comparison with that of other anions. It was decided to make a more detailed study of the effect of concentration of acetate and of temperature on the value of the potential. Moreover, it was shown recently by the present authors[5] that at low-current densities methane is also evolved along with ethane at the anode, and in investigating the conditions most favourable for the formation of methane the effect of varying anode potential is also of interest. The objects of this investigation were therefore :—

(1) To determine the " critical " potential for the formation of ethane during the electrolysis of aqueous potassium acetate solutions of varying concentration and at different temperatures.

(2) To see whether this ·potential is also a critical potential for the formation of methane which takes place along with that of ethane.

The determination of the critical potential was carried out by two methods, following the procedure of Preuner and Ludlam. Firstly, measurements were made of the current strength and of the anode potential during the electrolysis, and the resulting values plotted on a

[1] Bose, *Electrochem.*, **5**, 153, 1898.   [2] *Z. physikal. Chem.*, **59**, 682, 1907.
[3] *J.C.S.*, 3111, 1926; see also Walker, *J.C.S.*, 2040, 1928 (footnote).
[4] *Proc. Roy. Soc., Edin.*, **44**, 140, 1924; see also *J.C.S.*, **127**, 475, 1925.
[5] *Trans. Far. Soc.*, **27**, 35, 1931, referred to in text as Part I.

current density-anode potential graph.   The critical potential is indicated by a break or point of inflexion on the curve.   Secondly, samples of the anode gases were collected at different anode potentials and the particular potential found at which ethane is first evolved.   In many cases the gas samples were obtained during electrolyses in which the anode potential was measured directly as in the first method, but it was found to be more convenient, when the relationship between current density and anode potential had been determined for a given concentration of electrolyte, simply to collect the gas at a definite current density, from which the anode potential could be obtained.   The values of critical potential found by both of these ways coincided in nearly every case, and this can be taken therefore as a good example of a case where a break in the current potential curve does mark the commencement of a new reaction at the anode.   As will be seen from the current density-anode potential curves, and more readily from the log *C.D.*—anode potential curves, the break in the curve does not consist of a sudden sharp rise in the current density at a given potential, but rather of a small region in which the rate of increase of anode potential with current density becomes more rapid.

Experimental.

Apparatus.—The electrolyses were carried out in an H-shaped glass vessel, similar to that described by Gibson, in which the anode and cathode gases were collected in different compartments separated from one another by a thick plug of glass-wool.   The anode consisted of a smooth platinum wire, 4·4 cm. long and 0·1 cm. in diameter, and the cathode was a thin foil of platinum of 2 sq. cm. surface area.   A glass tube containing the same solution as the electrolysis vessel was pressed close up to the wire anode and connected through a solution of normal KCl to a normal calomel electrode, so that measurements were made of the *P.D.* of the cell

$$+ \text{ Pt.} \mid CH_3COOK \text{ sol.} \mid N \text{ KCl} \mid HgCl_2, N \text{ KCl} \mid Hg -$$
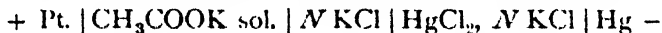
of which the mercury is the negative electrode.   By adding 0·283 volts, the potential difference between the anode and the solution (the anode potential, *A.P.*) on the hydrogen scale is obtained.   All the values in the tables refer to this scale.   No correction was made for liquid junction potentials, which are of the order of 0·01 volts when calculated by the formula of Lewis and Sargent.

A variable E.M.F. was applied across the terminals of the electrolysis vessel and successive readings of the polarising current and anode potential taken, time being allowed for these to become constant after every increase of the applied E.M.F.   In the preliminary experiments the solution was stirred during the anode potential measurements, but it was found that sufficiently reproducible results could be obtained with the stirring produced by the gases evolved—additional stirring simply has the effect of slightly lowering the anode potential for a given current density.   The first measurements were carried out at room temperature, which varied throughout the course of the whole work between 10° and 20° C., but was fairly constant during any single experiment.   However, in order to obtain more uniform curves and in order to study the effect of temperature variation, measurements were also made in which the electrolysis vessel was placed in a thermostat at temperatures of 5° ± 1°; 20° ± 0·1°; 35° ± 0·1° and 50 ±0·1° respectively.   Except where otherwise stated the solutions of potassium acetate contained an equivalent amount of added acetic acid to prevent the solution becoming alkaline during the course of the electrolysis.

Relation between Current Density and Anode Potential.

The values of current density and anode potential for solutions of potassium acetate of various concentrations at room temperature are plotted in Fig. 1. From these it will be seen that the current begins to rise rapidly at potentials between 2·0 and 2·3 volts and that on the whole the steepness of the curves decreases with increasing concentration of the electrolyte. In the case of the $N/5$ solution there is a noticeable break or point of inflexion in the curve at about 2·2 volts, which is not very apparent on the other curves. If, however, the log of current density is plotted against the $A.P.$ as has been done in Fig. 1a, the existence of a change in the slope of the straight line at about 2·15 volts is noticeable in almost every case. These
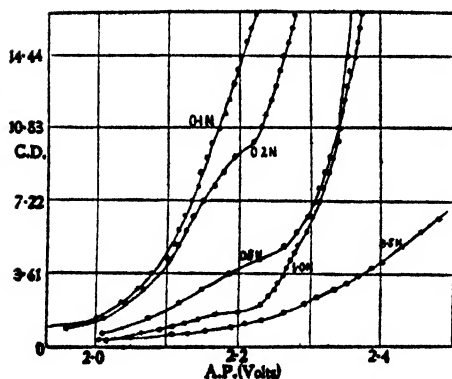
FIG. 1.
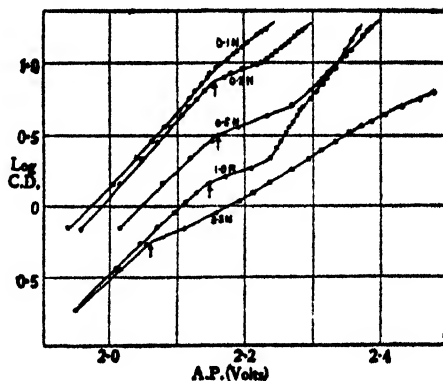
FIG. 1A.
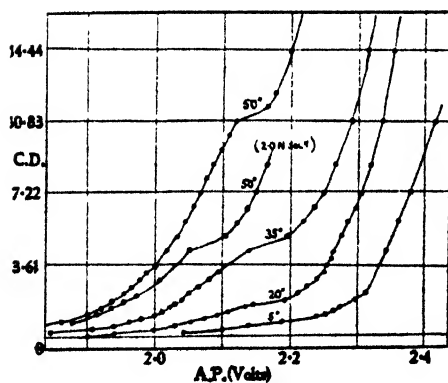
FIG. 2.
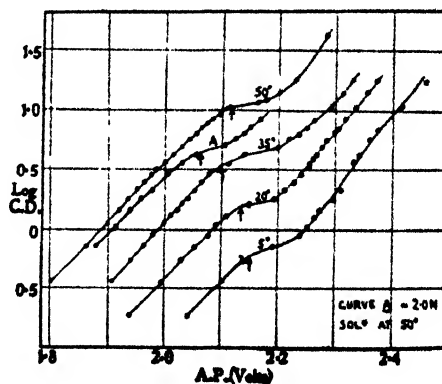
FIG. 2A.

experiments were performed at room temperature and not at a definite constant temperature. In the curves obtained from the experiments carried out in the thermostat, the existence of a break at 2·1-2·2 volts is very marked, as will be seen from Fig. 2 and particularly from Fig. 2a, in which the values for N potassium acetate at various constant temperatures are plotted. They contain also the curves for the 2 N solution at 50°. The breaks in the logarithmic curves consist of a decrease in the slope of the straight line within a small range of anode potential, the slope then resuming its original value. Within this small potential range the anode potential increases much more rapidly with increasing current density. Up to the

critical potential, *i.e.*, the potential at which the slope of the logarithmic curve changes, the relationship between the current density I and anode potential P is of the form,

$$P = a + b \log (I + c),$$

where a, b, and c are constants. Logarithmic relationships of this type have been found to hold for the evolution of hydrogen at certain cathodes and of oxygen at platinum anodes.[6] For two cases in which a large series of

TABLE I.

Conc. of Electrolyte.	Temp. °C.	Current Density Millamp. (per sq. cm.).	Anode Potential (volts).	Percentage of				Ratio $\dfrac{CH_4}{C_2H_6}$.
				CO_2.	O_2.	CH_4.	C_2H_6.	
0.2 N	10-20	3.61	2.09	2.5	93.5	0	0	—
		4.33	2.11	2.8	92.4	0	0	—
		5.05	2.12	33.7	41.0	2.6	15.9	0.16
		5.78	2.13	50.5	12.5	3.0	27.8	0.11
		7.22	2.15	49.2	4.3	3.3	36.8	0.09
1.0 N	5	0.72	2.19	16.3	72.4	0	0	—
		0.90	2.24	47.5	4.2	11.5	31.1	0.37
		1.26	2.26	56.9	1.3	6.4	31.3	0.21
		1.81	2.30	58.5	1.4	6.4	30.0	0.21
		3.61	2.33	55.8	1.2	3.5	34.9	0.10
1.0 N	20	1.44	2.13	20.0	70.0	0	0	—
		1.81	2.19	53.6	5.8	14.5	19.3	0.75
		3.61	2.25	53.3	1.7	5.2	35.7	0.15
1.0 N	35	1.81	2.04	13.8	80.7	0	0	—
		3.61	2.11	40.5	53.1	0	0	—
		5.05	2.20	57.9	7.4	8.3	17.6	0.47
1.0 N	50	10.82	2.12	32.7	55.8	0	0	—
		11.55	2.16	73.8	2.1	6.2	13.6	0.45
		18.05	2.23	75.4	1.5	3.7	14.1	0.26
2.0 N	50	1.44	1.94	27.9	65.4	0	0	—
		3.61	2.03	57.0	37.2	0	0	—
		5.05	2.11	74.0	2.1	8.3	11.8	0.70
		7.22	2.15	74.1	1.4	8.4	12.6	0.66
3.5 N	20	0.18	1.98	40.5	42.6	0	0	—
		0.36	2.04	46.1	1.5	32.8	9.3	3.53
		1.44	2.22	61.8	1.1	23.5	8.6	2.74
3.5 N	50	0.72	1.89	62.9	32.3	0	0	—
		1.44	1.95	68.9	23.3	0	0	—
		1.81	1.98	80.2	1.3	10.0	5.7	1.77

measurements are available in the region of *C.D.*, during which oxygen is evolved, *viz.* (1) for the $N/10$ solution at room temperature and (2) for the N solution at 50° the relationship holds almost exactly. The actual values of a, b, and c in these two cases are: (1) 1.922, 0.217, and 0.460, and (2) 1.870, 0.223, and 0.121, respectively. The maximum difference between observed and calculated values of the anode potential is 0.01 volt, but the difference is in general very much less, about 0.002-0.005 volt.

Glasstone, " The Electrochemistry of Solutions," page 381, 1931.

The values of the critical potential to the nearest 0·01 volt determined as the potential in the log *C.D.*/*A.P.* curve at which the slope of the line changes, have been tabulated in Table II. These potentials are indicated

TABLE Iᴀ.

Conc. of Electrolyte.	Current Density Milliamp. (per sq. cm.).	Anode Potential (Volts).	Percentage of		Ratio CH_4/C_2H_6.
			CH_4.	C_2H_6.	
0·5 *N* (room temp.)	2·88	2·15	0	0	—
	3·61	2·19	0	0	—
	4·33	2·23	9·0	34·2	0·26
	5·05	2 27	7·7	35·9	0·22
1·0 *N* (room temp.)	0·72	2·07	0	0	—
	1·44	2·15	0	0	—
	2·17	2·23	17·7	23·6	0·75
	3·61	2·26	7·7	32·9	0·23

on the curves by an arrow. In the case of the 3·5 *N* solution at 20° and 50° there was no definite critical potential on the curve. Before comparing these results with those obtained by the gas analysis method, the details of the latter method will be described.

Relation between Anode Potential and Composition of Anode Gases.

Samples of the gas evolved at the anode while the anode potential was kept constant at various values on either side of the critical potential were analysed for the following constituents: carbon dioxide, oxygen, carbon

TABLE II.

Concentration of Electrolyte	Temperature °C.	Critical Potentials.	
		Graphical Method.	Gas Analysis Method.
0·2 *N*	About 20	2·16	2·11
0·5 *N*	„	2·16	2·21
1·0 *N*	„	2·15	2·19
3·5 *N*	„	2·06	—
1·0 *N*	5	2·15	2·21
„	20	2·13	2·16
„	35	2·10	2·16
„	50	2·12	2·14
2·0 *N*	50	2·07	2·07
3·5 *N*	20	—	2·01
„	50	—	1·96
Average		2·12	2·16 (neglecting last two values)

monoxide, methane and ethane. The analyses were carried out by means of a Bone and Wheeler apparatus with mercury as the confining liquid, and the separation of methane from ethane was effected by means of liquid

air as already described by us.[7] The results of various experiments are shown in Table I., in which, to save space, only the percentages of carbon dioxide, oxygen, ethane and methane are given, since they illustrate the course of the main anodic reactions. The residue consisted of small amounts of carbon monoxide and of nitrogen from dissolved air. Table IA. contains some of the results of the previous paper (Part L), for which anode potential measurements are now available, and therefore only the percentages of ethane and methane are reproduced.

From the results of Tables I. and IA. the critical potential, i.e., the potential at which evolution of ethane commences, has been calculated and the values are tabulated, along with the values obtained by the graphical method, in Table II. The critical potential has been taken as the mean of the last measured potential at which no ethane is evolved and the first measured potential at which ethane is formed, e.g., in the case of the N solution at 20° no ethane is evolved at 2·13 volts, and 19·3 per cent. of ethane was found at 2·19 volts. The evolution of ethane must commence somewhere between these two potentials and therefore the mean of the two values, viz. 2·16 volts may be taken as the most accurate value of the critical potential.

Critical Potential for the Formation of Ethane.

In Table II. the values of the critical potential determined by the two methods are compared. It will be seen that the values obtained by both methods agree very well and that for very widely differing conditions of temperature and concentration of acetate there is very little variation in the potential at which ethane commences to be formed. The average value is 2·14 volts and is therefore considerably lower than Preuner and Ludlam's value of 2·54 volts. The variation from the mean value is seldom as large as 0·1 volt. Preuner and Ludlam, using the Nernst logarithmic expression, calculated the potential for a solution normal with respect to acetate ions, from their value of 2·54 volts obtained with a solution half normal with respect to both acetate and acetic acid, and obtained a value of 2·26 volts. From our results it is seen that in the concentration range 0·2 to 2·0 N there is very little variation in the critical potential. If this potential be assumed to be the discharge potential of the acetanions and to follow the Nernst concentration expression, no appreciable variation within this range is to be expected since a tenfold increase in the concentration, even assuming complete dissociation of the acetate, will decrease the discharge potential by about 0·06 volt only. With concentrations from 2·0 N upwards, however, there does appear to be a definite decrease of the potential, in agreement with the results of Fairweather and Walker,[3] who found that for 3, 4 and 5 normal solutions ethane formation takes place at lower anode potentials the more concentrated the solution. It is also seen that variation of the temperature does not greatly influence the potential at which evolution of ethane commences. As the temperature is increased, there is a small lowering of the critical potential, which is more marked in the more concentrated solutions.

Interpretation of the Critical Potential.

It has thus been established that at a smooth platinum anode a break in the current potential curve and the commencement of ethane evolution both occur at a potential of 2·14 volts, and that this potential is only

[7] Walker and Shukla, *J.C.S.*, 368, 1931 ; see also Part I.

slightly influenced by the temperature and by the concentration of acetate in the solution.   At this anode potential a new reaction evidently begins to take place and the potential may be explained in three ways:

(1) Potential at which the reaction,

$$2CH_3COOH + O = C_2H_6 + 2CO_2 + H_2O \qquad . \qquad . \quad (1)$$
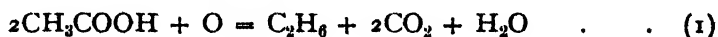
commences.

(2) Discharge potential of the acetanions.

(3) Potential at which discharged acetate ions cease to react with water and commence to react with one another.

The first interpretation has generally been favoured by the supporters of the oxidation theory of Kolbe's reaction, but this view is in our opinion open to certain objections (see Part I.).   Preuner and Ludlam adopted the second view and considered it to be evidence for the discharged anion theory that evolution of ethane does not commence till a definite potential is reached.   Their value of 2·54 volts has been generally given in the literature and text-books as the discharge or decomposition potential of the acetate ion.   If this view is correct the evolution of oxygen below the critical potential must be ascribed to the discharge of hydroxyl or oxygen ions.   There is, however, no conclusive evidence for this assumption, which is also open to criticism (see Part I.), and it seems just as probable that below the critical potential acetate ions are being discharged, and that the change in the anode reaction consists merely in the change from

$$2CH_3COO + H_2O = 2CH_3COOH + O \qquad . \qquad . \quad (2)$$
$$\text{to} \qquad\qquad 2CH_3COO = C_2H_6 + 2CO_2 \qquad . \qquad . \qquad . \quad (3)$$
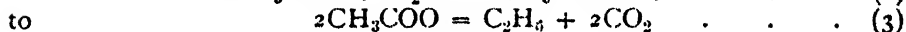
In fact the nature of the break in the current-potential curve might be taken to support this view, since it does not consist of a sudden rise in the current such as occurs in the discharge of a new ion species at a definite potential, *e.g.* in the cathodic discharge of metallic ions.   A definite decision as to the meaning of the critical potential is not possible, however, and all one can say is that at that potential, whether it is a true discharge potential or not, a new reaction occurs.   The results described do show, however, that the primary factor in determining the commencement of the anodic process is the anode potential, and not the particular value of the current density which is only of secondary importance.   For example in the concentration range 0·2 to 2·0 N between 5° and 50° ethane evolution may commence at current densities between 0·9 and 11·6 milliamperes per sq. cm., depending on the particular conditions, whereas the anode potential at which the ethane reaction begins is constant at about 2·14 volts.   It is possible that the anode potential corresponds to a definite concentration of discharged ions at the anode surface, and that not until this concentration of discharged ions is reached can they react together to form ethane.   A large concentration of acetate in the solution, and low temperature both favour the formation of ethane, and that is because both these factors have the effect of increasing the anode potential for a given current density.   Increase in current density after the critical potential has been reached will still further increase the anode potential and therefore increase the yield of ethane (*cf.* Fairweather and Walker, *loc. cit.*[3], page 3114).

Formation of Methane.

So far only the formation of ethane has been considered, but the experiments described in this paper also provide further information re-

garding the production of methane.   The most convenient method of comparing the various experiments is to examine the ratio of methane to ethane.   The results of Table I. confirm the observations previously made that the first appearance of methane in the anode gases occurs along with that of ethane, and it may now be said that both these hydrocarbons commence to be formed at the same critical potential of 2·14 volts, at which the amount of oxygen evolved drops to a small percentage.   Whereas, however, the amount of ethane formed above this anode potential increases with increasing current density until it reaches a maximum value of about 90 per cent. of that theoretically possible,[3] the amount of methane appears to be at a maximum at the point where it is first formed and rapidly decreases with increasing current density, as is clearly seen from Tables I. and IA.   In the results given in Part I.,[5] the highest value of the methane/ethane ratio was 1·89.   In the further experiments of Table I. values as high as 3·5 have been obtained.   The following series of electrolyses at low current densities of a 3·5 N solution at about 10° illustrate even more clearly the decrease of the CH_4/C_2H_6 ratio with increasing current density (Table III.).

TABLE III.

Conc. of Electrolyte.	Current Density in (Milliamp. per sq. cm.).	Percentage of.				Ratio CH_4/C_2H_6.
		CO_2.	O_2.	CH_4.	C_2H_6.	
	0·18	35·6	1·2	41·5	9·8	4·3
	0·29	33·8	2·6	46·1	9·4	4·9
	0·72	55·0	0·5	32·2	7·9	4·1
3·5 N	1·44	53·0	0·8	29·8	9·9	3·0
(about 10° C)	2·17	73·0	0·2	15·8	8·6	1·84
	3·6	66·9	0·9	16·8	11·5	1·45
	7·22	70·0	0·7	4·1	21·1	0·19
	10·82	64·7	1·8	2·2	27·6	0·08
9·9 N	0·72	0	1·5	65·8	22·0	2·99
(about 10° C)	1·81	0·3	0	12·3	79·2	0·16

In order to see whether the ratio methane/ethane could be still further increased by increasing the acetate concentration a 9·9 N solution of potassium acetate (without added acetic acid) was electrolysed using a large platinum foil anode (14 sq. cm. surface area, waxed on one side) so that even smaller current densities might be used.   The results are given in Table III.   At a current density of 0·07 milliamps. per sq. cm. only three times as much methane as ethane was obtained, but the solution was appreciably alkaline through hydrolysis in this case, as is seen from the absence of carbon dioxide.   It appears, therefore, from all the experiments made that the ratio methane/ethane has a maximum value at the critical potential, the maximum being greater the higher the concentration of the solution.   The effect of acetate concentration is best seen by comparing values of the ratio taken from Table I. at the lowest current density in each case at which hydrocarbons are formed, i.e., at a potential just slightly higher than the critical potential :

Conc. of sol.	.	.	.	0·2 N	0·5 N	1·0 N	3·5 N
A.P.	.	.	.	2·116	2·19-2·23	2·23	2·04
CH_4/C_2H_6	.	.	.	0·16	0·41-0·26	0·75	3·5-4·9

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Conclusion and Summary.

The conditions for the formation of ethane and methane at a smooth platinum anode during the electrolysis of aqueous potassium acetate solutions have been more closely defined as a result of the experiments described in this paper. The results may be summarised as follows :—

(1) Below an anode potential of $2 \cdot 14$ volts oxygen and carbon dioxide are the main gaseous products, and no hydrocarbons are evolved.

(2) At the critical potential of $2 \cdot 14$ volts methane and ethane commence to be formed along with a larger amount of carbon dioxide, and the proportion of oxygen begins to decrease rapidly. There is not sufficient evidence to show whether this critical potential represents a true discharge potential of the acetanion.

(3) For concentrations of acetate below $2 \cdot 0$ N the critical potential is independent of concentration, but with more concentrated solutions the value decreases. The critical potential decreases slightly with increase of temperature.

(4) At the critical potential the ratio methane to ethane is at a maximum, and then decreases rapidly with increasing current density, so that methane is formed only within a limited range of current density. The maximum value of methane/ethane increases with the concentration of acetate. With a $3 \cdot 5$ N solution under the most favourable conditions a value of nearly $5 : 1$ was obtained.

Of particular interest is the question of how the methane is formed. Certain possibilities were indicated in Part I., but a more detailed discussion of the problem will be held over until the conclusion of some further experiments now in progress on the influence of dissolved substances and of the solvent on the formation of methane.

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THE EFFECT OF PHOSPHORUS VAPOUR ON REACTIONS BETWEEN INCANDESCENT TUNGSTEN, WATER VAPOUR AND OXYGEN IN THE PRESENCE OF AN INERT GAS.

By J. T. Randall, M.Sc., and J. H. Shaylor.

The reaction between incandescent tungsten and water vapour has been investigated by Langmuir [1] and Smithells.[2] According to the former, tungsten combines with the oxygen of the water vapour and the resulting oxide evaporates on to the bulb, where it is reduced by atomic hydrogen formed at the filament surface. The filament is again attacked by the water vapour formed; the reaction is cyclic and has disastrous effects on the life of a filament. Phosphorus, as is well known, is used as a "getter" in vacuum lamps, that is, an aid to the production of a very much lower pressure than that achieved by the pumping system alone. The red phosphorus is applied to the filament so that, on lighting up the pumped

[1] I. Langmuir, *Proc. Am. Inst. Elec. Eng.*, **32**, 1893, 1913.
[2] C. J. Smithells, *Trans. Faraday Soc.*, **17**, 485, 1921.

lamp the phosphorus is rapidly evaporated and takes part in an electric discharge which is essential to the " clean-up " process.[3] It has also been customary to use phosphorus in a gas-filled lamp, although the reasons for its use are obscure and, so far as we are aware, no work has been published on this. It has been clear to those who habitually manufacture gas-filled lamps, however, that the effect of phosphorus, if any, was connected with the inhibition of the oxidation of the filament by residual gases. Whether the effect was " chemical " or " physical " was not known. The following is a brief account of experiments made to determine the precise nature of the reaction.

1. Experimental.

Use has been made of the fact that the resistance of a wire changes when it has been subjected to chemical attack. 220 volt 40 watt gas-filled lamp filaments of pure tungsten were mounted in ordinary lamp bulbs in the usual way. Some of the filaments had previously been dipped in a solution of red phosphorus after dyeing. The mass of phosphorus on the filament was determined accurately by weighing on a torsion balance. Attached to the pumping system were supplies of water vapour and oxygen and a Pirani gauge for measuring pressures. After pumping and baking, a lamp was filled with (say) 0·1 mm. water vapour. 400 mm. of an 80 per cent. argon-nitrogen mixture were then slowly added and equilibrium between the vapour and gases was allowed to set in. The lamp was then sealed-off and almost completely immersed in a large bath of cold water. The " cold " resistance of the wire was then determined by means of a low resistance galvanometer and Wheatstone Bridge. The progress of the reaction was followed by (say) burning the lamp at its normal running temperature (about 2600° K) for two minutes, allowing the gas and filament to cool, measuring the " cold " resistance again, and so on.

2. Results.

(a) **Tungsten and Water Vapour.**--In Fig. 1 are plotted curves connecting the " cold " resistance of coiled tungsten wires against time of burning in the presence of water vapour and inert gas. The resistance of the wire always falls several per cent. during the first minute of burning owing to recrystallisation of the tungsten (Curve (a)). This is a feature common to many metals. After burning for twenty minutes or so the recrystallisation process is completed and the resistance remains steady. Small quantities of water vapour (0·01 and 0·025 mm.) have no appreciable effect on the shape of the curve within the errors of measurement. Fig. 1(c), however (0·05 mm. H_2O) shows a marked change.* After first falling in the familiar way the resistance then rises, as we should expect, due to uniform thinning caused by oxidation. This rise becomes progressively bigger for increasing quantities of water vapour. Knowing the mass of the filament the amount of tungsten consumed can be calculated ; the pressure of water and volume of bulb give the quantity of oxygen. If it is assumed that no water is given off by the glass walls the calculation leads us to the conclusion that a compound WO is formed. It is true that a more complex reaction might lead to the ratio W : O being 1 : 1 without any compound WO being formed. For this, however, cyclic reaction would have

[3] N. R Campbell, *Phil. Mag.*, 40, 585, 1920, and other papers.
* It is possible that reaction with surface impurities makes the quantity of water vapour introduced effectively less. One would have expected 0·025 mm. H_2O to have given a measurable change in resistance.
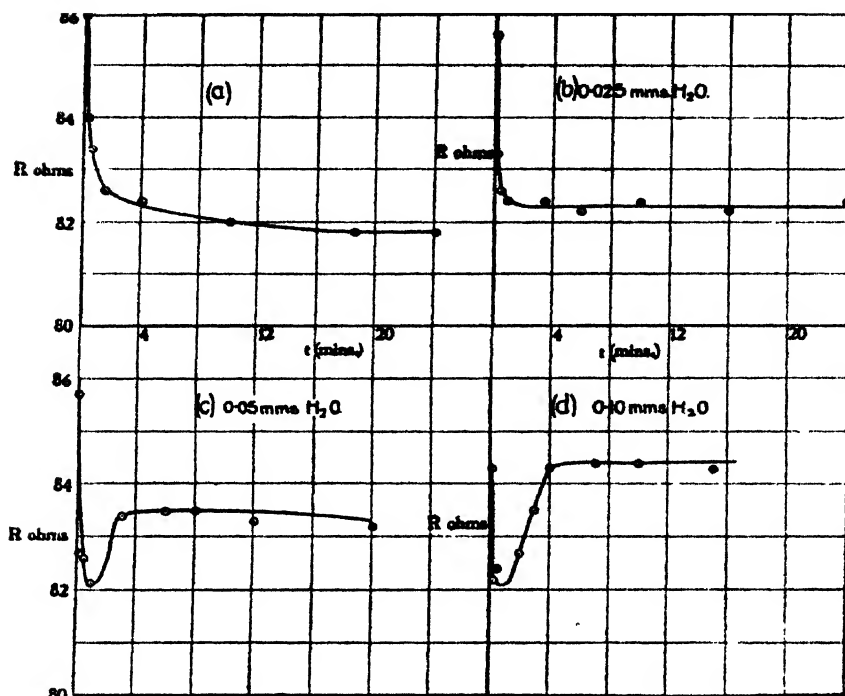
Fig. 1.
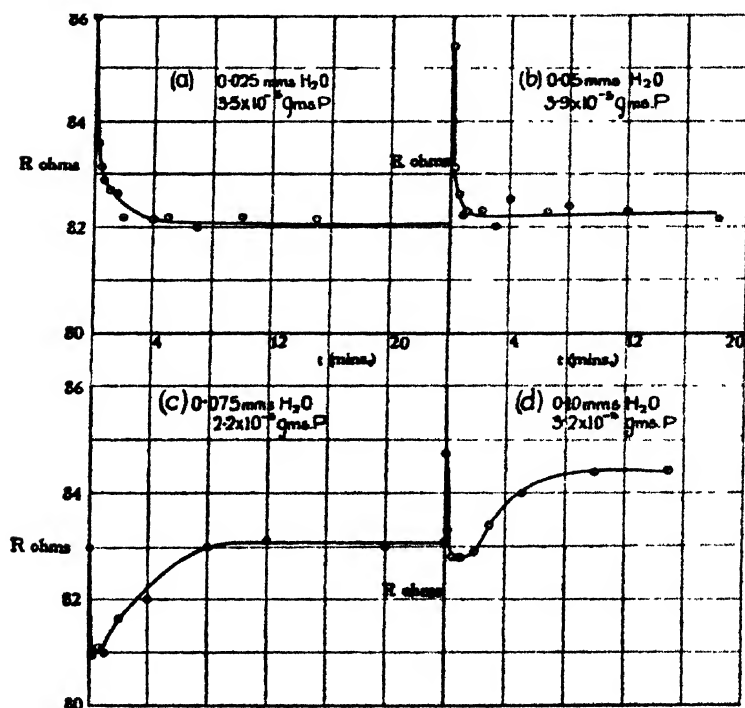
Fig. 2.

to take place in the first few minutes of burning. The curves, however, show that the particular reaction which we are considering is completed in a few minutes. Had the cyclic reaction played a major rôle the filaments would have failed in this short interval of time which was never found to be the case. All the evidence points, therefore, to the formation of WO. It must be emphasised, however, that it is impossible to be absolutely certain of the W/O ratio on account of the possible evolution of sorbed water vapour from the bulb. The simple mechanism only of the reaction is stressed.

(*b*) **Tungsten, Water Vapour, and Phosphorus.**—The phosphorus was introduced into the lamp in the manner already described. Fig. 2(*b*) which should be compared with Fig. 1(*c*), shows that the phosphorus has interfered with the oxidation of the filament by H_2O. The effect is readily explained if we assume that the phosphorus, diffused throughout the inert gas in the neighbourhood of the filament, combines with the oxygen of the water vapour. This explanation is justified by the fact that heats of reaction of P—O compounds are greater than those of W—O compounds. The exact mechanism of the reaction is unknown but it is not unlikely that the H_2O is first dissociated by the hot tungsten before the P—O reaction sets in. It must be emphasised that the whole cycle of events depends on the presence of the inert gas. For otherwise the phosphorus would not remain in the active form for any appreciable length of time. This was tested in the following experiment. In order to avoid the complications arising on the passage of an electric discharge between two ends of an ordinary 200 volt lamp filament in H_2O at low pressure, a short tungsten filament requiring about 10 volts to raise it to 2600° K was coated with red phosphorus and mounted in a bulb. On lighting the filament in the presence of water vapour (several hundredths of a mm.) the bulb was *immediately* covered with a deposit of inactive phosphorus. There was no difference between initial and final pressures of water vapour. Experiments on high frequency discharges through the filling of a gasfilled lamp have shown that the "life" of a small quantity of phosphorus vapour is of the order of minutes when the filament is burning. As the resistance curves show this is the order of time required for the completion of the reaction. Figs. 2(*c*) and 2(*d*) show the effect of phosphorus for increasing quantities of H_2O and it appears that, within the limits of the experiments, a definite ratio of combination of P and O exists. These observations, and many others not included here, suggest that 3 atoms of P combine with one of O, to the nearest whole number. The calculated P/O ratio was 3·2. After the weight of phosphorus has been determined by the torsion balance, the filament has, of course, to be mounted in supports and a little phosphorus may have been lost in this way, but care was taken to reduce this to a minimum. If any phosphorus were lost it would suggest that P/O = 3/1 rather than 4/1.

It has also been shown that the curves for W—O_2 are qualitatively of the same type as those for W—H_2O. The quantitative difference between the two reactions in the presence of an inert gas can be gathered from Fig. 3 where percentage change of resistance is plotted against *p* for H_2O and O_2. The large difference between the slopes of the two curves can be explained if we assume that higher oxides are being formed when oxygen is an impurity.

Such curves as those of Fig. 3 are difficult to obtain with accuracy and it would be dangerous to stress the quantitative aspect. Roughly speaking, however, it may be said that H_2O under these conditions combines with W to form WO + H_2. The slightly increasing slope of the H_2O curve with

increasing amount of H_2O possibly indicates that the water vapour absorbed by the bulb in the initial filling of the lamp is being given off during the reaction. There are two reasons for this: (a) heating of the bulb by hot gas and radiation from the filament, (b) upset of equilibrium between free and sorbed H_2O. There is, at any rate, no evidence to show that an oxide higher than WO is formed.

In the case of $W—O_2$ reaction apparently no oxide lower than WO_2 is formed. At pressures of o·2 mm. O_2 the curve suggests WO_4 but the experiments are not sufficiently accurate to distinguish between this and the well-known WO_3. The "wreath" filament of a gas-filled lamp is supported by molybdenum wires at various points of its length and these become coated with the products of reaction during the experiments. In the hope of confirming the above ideas of oxide formation these deposits were examined by
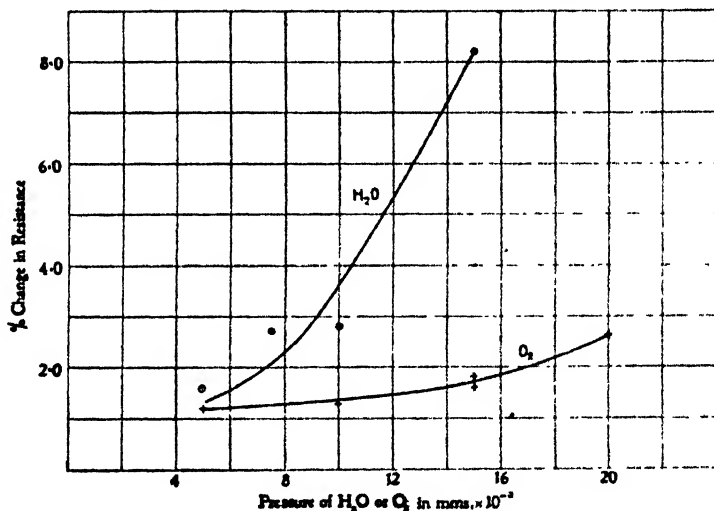
FIG. 3.

X-rays. For all the smaller pressures, however, the photographs indicated tungsten alone and only at o·2 mm. O_2 did WO_2 show up. If, therefore, tungsten is stripped from the filament by oxygen in the proportions already suggested, the resulting oxides are

(a) unstable, i.e. the heat is sufficient to break down the compounds and the oxygen is held by forces of adsorption, or

(b) they are reduced by the hot molybdenum support wires.

It is evident that the oxygen is held either by the tungsten or molybdenum for there is never any sign of the cyclic reaction which would take place if the oxygen were set free to attack the filament again. From these remarks it follows that the details of the $W—O_2$ reaction are not so simple as has hitherto been supposed. It should be possible to test out the idea of the reduction of tungsten oxides by molybdenum by using tungsten support wires We hope to carry out this work in the near future.

Summary.

It is well known that the evaporation of red phosphorous from the filament of a vacuum lamp leads, through the agency of an electrical discharge, to the production of a higher vacuum than would otherwise be possible without the use of very elaborate technique. Not so well known is the fact that phosphorus is

also used in gasfilled lamps. The object of this paper is to try to explain its action. If H_2O is originally present in the gasfilling, the yellow phosphorus produced on the initial lighting of the filament combines with the oxygen of the water-vapour, forming (probably) P_3O. Thus the ordinary cyclic reaction between tungsten and water vapour is, so far as the limits of these experiments show, prevented. The presence of the inert gas is essential to the phenomenon since, *in vacuo*, the yellow phosphorus vapour would be immediately deposited on the glass walls as the inactive red variety.

Experiments have shown that as the quantity of O_2 as an impurity increases, increasingly higher oxides of tungsten are formed, whereas (again within the limits of the experiments) the only oxide formed in the presence of water vapour appears to be WO.

REVIEWS OF BOOKS.

An Early Experiment in Industrial Organisation, being a History of the Firm of Boulton & Watt, 1775-1805. By ERICH ROLL, B.Com., Ph.D. (Birm.). (London : Longmans, Green & Co., 1930. Pp. xii and 315. Price 15s. net.)

Dr. Roll has produced a fascinating study of the rise and development of the firm of Boulton & Watt. The first part of the period covers the twenty-five years' extended life of the Watt patent, and shows how the partners, in anticipation of the cessation of their monopoly, prepared themselves for the inevitable period of intense competition by a degree of scientific organisation of their factory methods which was many years ahead of anything else to be found in the country. The book is well written in an easy style. It well repays close study.

Adventures in Biophysics. By A. V. HILL, Sc.D., LL.D., M.D., F.R.S (Oxford University Press, 1931. Pp. 162. 7 Figs. 12s. 6d.)

Professor A. V. Hill's book entitled "Adventures in Biophysics" enables readers to enjoy the lectures for the Eldridge Reeves Johnson Foundation for Medical Physics which he gave in Philadelphia in 1930. To those interested in muscle activity the book gives an invaluable survey of the latest researches in that field. To those unacquainted with the problems of physiology an opportunity is here afforded of reading a clear and brief account of ingenious applications of physical technique. The thermal method of comparing vapour pressures, which can be made to give a 1000 mm. galvanometer deflection for the difference of vapour pressure between water and 1 per cent. NaCl, may not yet be widely known outside biological circles. Unfortunately such a topical book soon becomes out of date, especially as research in this field is so active. Nevertheless we are grateful to Professor Hill for having drawn up this temporary guide to the positions of the battalions on the battlefield.

A Text-book of Experimental Cytology. By JAMES GRAY. (Cambridge University Press, 1931. Pp. 516. 205 Figs. Price 25s.)

The problem of the cell as a biological unit, and as a physico-chemical colloidal system is of such fundamental significance that it will continue to attract the attention of biologists and physical chemists certainly for decades, and probably for centuries. Dr. Gray has collected the data which is known at present in this text-book, and has given full references to the original papers. The figures are plentiful and exceptionally clear.

Chemisches Fachwörterbuch für Wissenschaft, Technik und Handel.   By
    A. W. MEYER.   Bd. II. Englisch-Deutsch-Französisch.   (Leipzig, Verlag
    von Otto Spamer, 1931.   Pp. 943.   Price 75 Rm.   Cloth bound.)

The first volume of this work, which the reviewer has found very useful, was
noticed in these columns (vol. 26, p. 263).   The author has kept in volume 2 to
the general scheme used for the first volume, but has incorporated several improve-
ments with a view to removing ambiguities in the explanatory text.   It is feared
that some prospective purchasers may be somewhat deterred by the occasionally
unusual phrasing of the English preface, and it would perhaps have been well if
this had been edited by an Englishman in England—the reviewer's experience
indicates that, no matter how good an English scholar a German may be, it is
very exceptional to find one whose writings do not betray him ; even Englishmen
resident in Germany tend to think teutonically.   If, however, the buyer will spend
some time in perusing the dictionary itself, he will appreciate the real value of the
work and will see that the author clearly distinguishes between shades of meaning.
After all, what is needed in this volume is a correct appreciation of the proper
counterpart of English words, so that it would be harsh to judge the volume on its
preface.
    The author is unashamed (and, in the reviewer's more extended experience
of the first volume, justifiedly so) of his policy of prolixity rather than time-wasting
cross-reference.   Dictionaries of this type are not intended for the coat pocket, so
that the only disadvantage accruing from this policy is the necessary bulk and the
consequent price.   As the author points out, however, the resulting saving of time
to the user justifies the policy and the price.   The book is admirably produced.

A Survey of Physics.   By FREDERICK Q. SAUNDERS.   (London : G. Bell
    & Sons.   Pp. x and 643.   Price 14s. net.)

Professor Saunders has provided an admirable summary of all branches of
modern physics ; it is intended primarily for the junior university student but is
readily understandable by any reasonably educated person who desires to know
something of modern ideas.   The principles are frequently illustrated by examples
of the kind one has seen at the end of the *Strand* magazine, so that the interest of
the young student is held.   The arrangement of the book is logical and the exposi-
tion smooth and clear ; the illustrations are admirably chosen and well reproduced.

Chemistry in the Service of Man.   By ALEXANDER FINDLAY.   Fourth
    Edition.   (London : Longmans, Green & Co. Ltd.   Pp. xviii and 355.
    Price 6s. net.)

It is sufficient to remind readers that this is the fourth edition of Professor
Findlay's popular work produced since 1916.   The opportunity has been taken
to revise the book and bring it up-to-date.

The Mysterious Universe.   By Sir JAMES JEANS.   Second Edition.   (Cam-
    bridge : The University Press.   Pp. ix and 142.   Price 2s. net.)

Sir James Jeans is now an established " best-seller ! "   The first edition was
reprinted six times and now we have a second edition at popular prices !   Its
success is the book's sufficient commendation.

ON THE PASSIVITY OF METALS.

By Professor Dr. W. J. Müller, *Vienna*.

A LECTURE

(Given before the Faraday Society in London on 18th September, 1931).

A metal is described as passive if it is only slightly or not at all attacked either when acting as an anode in an electric circuit, or when treated with chemical reagents. It is described as active when, under the same conditions, it is vigorously attacked. Special interest is attached to those cases where, according to the conditions, a metal shows either an active or a passive reaction. Such cases were first demonstrated by Keir at the end of the eighteenth century in the action of iron on a silver nitrate solution acidified with nitric acid. The observations of Keir sank into oblivion and the peculiar reaction of iron with nitric acid was investigated later by Wetzlar, and more particularly by Schönbein who introduced the terms activity and passivity. Fechner discovered that iron could be either active or passive when acting as an anode. This was further pursued by Schönbein who showed by most ingenious experiments that iron is rendered passive in concentrated nitric acid through the action of local effects. Schonbein believed that passivity was brought about by a change in the metal itself. Faraday, to whom Schönbein communicated his observations, established in his famous letter the theory that the passive condition was brought about by a film of oxide, or by a similar state of affairs. In Germany, Betz upheld this theory, but Schönbein persisted in his own view.

After numerous experiments on passivity had been made, and still more theoretical views had been published, in the forties and fifties of the last century, the question was dropped until the nineties when Hittorf published his famous experiments on chromium, particular in regard to anodic passivity. Hittorf, as a result of his experiments on chromium and other metals, came to the conclusion that the assumption of an oxide layer was not sufficient to explain the many diverse phenomena of passivity, but that these could be better explained through a "*Zwangszustand*" of the metal in the passive state. Explanations of this "Zwangszustand" were supplied by Krüger and Finkelstein who assumed that a metal differs in its state of valency according as to whether it is active or passive. Shortly afterwards, the author attempted to explain the difference of state on the basis of the electron theory of metals. Other attempts at explanation were made by Leblanc, and in support of his views Sakur assumed that the primary anodic process consisted in the discharge of anions. If the action of the discharged anion is hindered through any influence of a catalytic nature, the metal becomes passive. Fredenhagen accepted the idea, first expressed by Belk, that passivity is brought about by an oxygen film which is formed electrolytically. Haber and his school modified the original view of Faraday by stating that the passive reaction of a metal was caused

by a film of oxide, but that this film consisted of transient pores. When the pores are closed the metal is passive, and when open it is active. Experiments made by the author and Koenigsberger, using optical methods (measurement of the power of reflection in the active and passive state), with the object of differentiating between the theories, showed that in the cases investigated no change in the power of reflection was shown. It might, however, be objected in regard to these experiments that the persisting oxide film could explain this condition just as well as the assumption of a change in state of the metal.

An objection against the electronic theory of the author was raised by Fredenhagen, who suggested that such a displacement of electrons in the metal signifies a greater expenditure of work, which cannot be accounted for by the current density which causes the passivity. Foerster put forward the theory that the "active" behaviour of iron is caused by the adsorption of hydrogen but, however, he soon relinquished this theory. He distinguished between mechanical passivity which is caused by a visible film (magnesium, aluminium, etc.) and chemical passivity in which there is no visible film.

The metal theory found another supporter in Smits who assumed that the anodic charge causes a displacement in the equilibrium of the electrons in the metal, characterised as a distortion (*Verstörung*). (The author also assumed this.) If this condition remains metastable the distorted metal shows a passive reaction.

All these attempts at explanation were of a purely hypothetical and qualitative nature, and did not make it possible to reproduce the phenomena of passivity in a quantitative manner.

Some light was thrown on the subject by the experiments of the author on thallium which had been anodically rendered passive. It was shown that thallium went "actively" into solution as the anode in an $N/10$ solution of caustic soda, even at high current densities, whereas in N caustic soda solution, even at low current densities it became passive, with the appearance of a visible white film. The passive thallium went into solution in the divalent condition, but hydrolysed to thallium trioxide and thallium monoxide, the former causing a further passivity, with evolution of oxygen at the anode. The author's explanation of these experiments is that the thallium is at first covered with a layer of thallium monohydroxide (which is difficultly soluble in N caustic soda), through which the current density rises on the remaining metal surfaces and reaches a value which owing to the displacement of electrons, causes a transformation of the thallium metal from the mono- to the divalent state. This causes the thallium to go into solution in the divalent state, which decomposes into thallium trioxide, and thallium monoxide, the former producing a protective conducting layer, the latter going into solution.

The further development of these trains of thought led in the year 1922 to the cinematographic study of the anodic process of passivity in sodium sulphate solution. This showed that iron, subjected to an electric current remains active for some time, after which it becomes passive—as could be seen from the evolution of oxygen and the smooth appearance of the electrode, and the precipitation from the electrode of thick striae which could only originate in a relatively easily soluble layer already present. This relatively easily soluble layer needs some time to develop. Thus, the phenomenon of anodic passivity was characterised as a time phenomenon, and further explanation was left to the realm of kinetics. For this purpose we must avail ourselves of strict experimental conditions. In all previous

experiments on passivity use was made of electrodes which hang freely in the solution.   Since on anodic attack concentrated solutions of the salts in question are generally formed directly at the anode and fall therefrom (as I have shown above) in the form of striae, passivation only arises at those current densities at which the local concentration becomes so large that the deposited layer falls away spontaneously.   For this reason we believed that passivation is characterised by a definite upper limit of current density, which we designate the *passivating current density*.   In order to attain strictly satisfactory experimental conditions, the electrodes must be so formed that the layer which builds up on the anode is not removed by convection effects at all, but only by diffusion and migration.   This was attained experimentally by the use of the "shielded electrode," Fig. 1.

A spiral metallic cylinder (*b'*) which is connected at its lower end to a leading-in wire (*b*) contained in a bent glass tube (*a*) is compressed by a metal cylinder (*c*) which is kept in position by a piece of rubber tubing (*d*) which overlaps the cylinder and the glass tube and makes a tight fit. The upper metal surface is kept horizontal.   In this
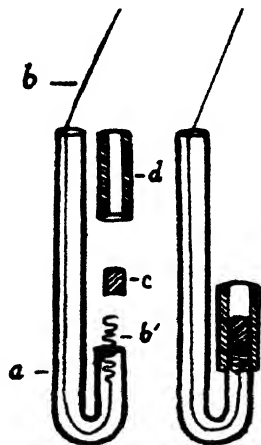
Fig. 1

way we ensure firstly that the current reaches the metal parallel and secondly that the above-mentioned condition of excluding convection is fulfilled.

A relationship which served to explain the covering of a metal electrode in a solution saturated with the reaction products was derived theoretically. This gave the formula,[1]

$$t = C + A\left(\frac{1}{i_0 - i} + \frac{2\cdot3}{i_0} \log \frac{i_0 - i}{i}\right) . \qquad . \qquad . \quad (1)$$
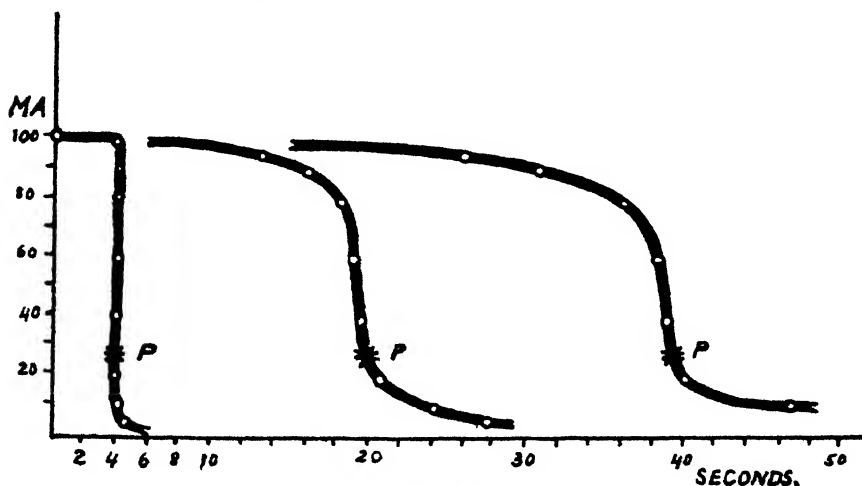
Fig. 2.

[1] *Explanation of symbols* : —

t = Time.
F = Surface.
δ = Thickness of film.
E = Electromotive force.
ϵ = Single electrode potential referred to N hydrogen electrode.

i = Strength of current in amperes.
w = Resistance in ohms.
k = Faraday constant.
u = Transport number of the anion.
κ = Specific conductivity.

which represents the time taken for such a layer to form. The constants

$$C = \frac{s\delta}{k(1 - u)} \frac{F_0}{i_0} \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

$$A = \frac{s\delta^2}{\kappa k(1 - u)w_0} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

contain only absolute fundamental units. The relationship was shown to hold for a large series of cases with iron, nickel, zinc and copper.

In Fig. 2 we see the form of current-time curve which the relationship requires, and in Figs. 3 and 4 are given the curves for iron.
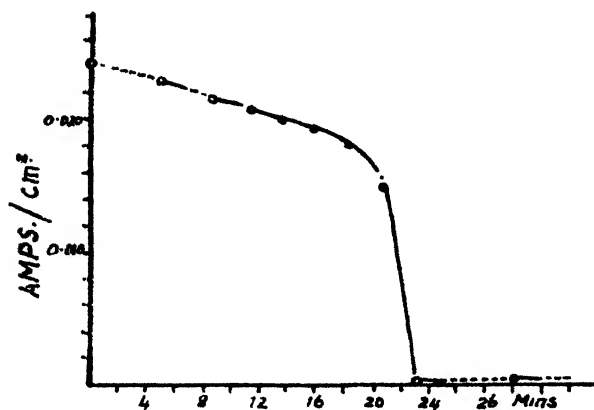
Table I. shows the calculation of the constant A in the case of iron, Table II. in the case of copper and Table III. the conductivity of the electrolyte in the pores calculated from the constants A and C.

FIG. 4.—2·0 N H_2SO_4.

TABLE I.—IRON IN ACID FERROSO-FERRIC SOLUTION.

(0·5 cm.^{2}; 11 ohms; 20 C.; $i_0 = 0.098$.

t.	i.	$i_0 - i$.	H.	L.	e	$C - t$.	$A \times 10^8$.
19·000	0·0926	0·0054	− 185	− 28	− 213	+ 4·417	2·08
19·684	0·0914	0·0066	− 152	− 26	− 178	+ 3·733	2·10
20·368	0·0885	0·0095	− 105	− 21	− 126	+ 3·049	2·42
21·052	0·087	0·010	− 91	− 20	− 111	+ 2·365	2·13
21·394	0·0856	0·0124	− 81	− 19	− 100	+ 2·023	2·02
21·736	0·0841	0·0129	− 72	− 17	− 89	+ 1·681	1·89
22·078	0·0812	0·0186	− 59·5	− 15	− 74·5	+ 1·339	1·80

$C = 23·417$.

TABLE II.—COPPER IN N H_2SO_4

t.	i.	$i_0 - i$.	$i - i_r$.	H.	L.	e.	$C - t$.	$A \times 10^8$.
13·000	0·1695	0·0035	0·1675	− 285·7	− 22·4	− 308·1	+ 4·965	1·61
13·333	0·1670	0·0060	0·1650	− 166·7	− 19·1	− 185·8	+ 3·632	1·92
15·667	0·1640	0·0090	0·1620	− 111·1	− 16·7	− 127·8	+ 2·295	1·79
17·000	0·1520	0·0210	0·1500	− 47·6	− 11·3	− 58·9	+ 0·965	1·64
17·267	0·1430	0·0300	0·1410	− 33·3	− 8·9	− 42·2	+ 0·698	1·65
17·534	0·1270	0·0460	0·1250	− 21·8	− 5·8	− 27·6	+ 0·431	1·56
17·854	0·0740	0·099	0·720	− 10·1	+ 1·84	− 8·73	+ 0·111	1·35
17·934	0·0500	0·123	0·048	− 8·13	+ 5·43	− 2·70	+ 0·031	(1·15)
17·986	0·032	0·141	0·030	− 7·08	+ 8·94	+ 1·86	− 0·021	(1·14)
18·093	0·013	0·160	0·011	− 6·24	+ 15·47	+ 9·23	− 0·128	1·39
18·147	0·0098	0·162	0·0078	− 6·2	+ 17·6	+ 11·4	− 0·182	1·60
18·202	0·0062	0·167	0·0042	− 6·1	+ 21·2	+ 15·2	− 0·237	1·56

$C = 17·965.$
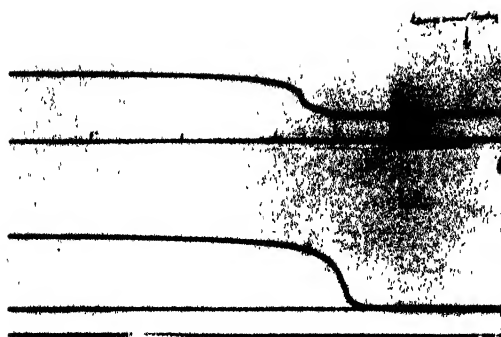
FIG. 3.

See page 740.
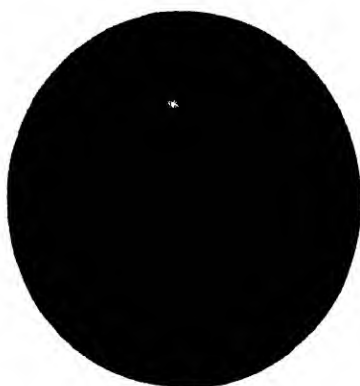
FIG. 5.

See page 741.
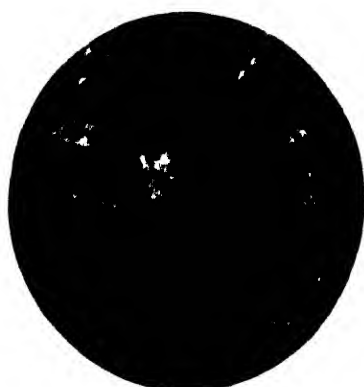
FIG. 6.

FIG. 7.

FIG. 8.

FIG. 9.

See page 741.
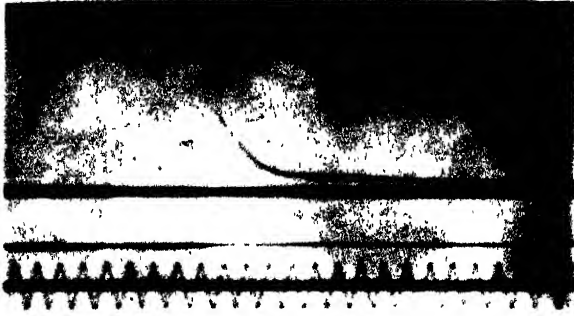
FIG. 18.
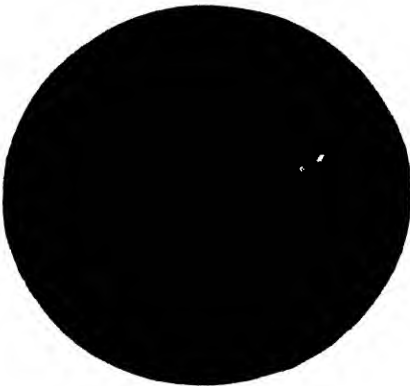
FIG. 19.
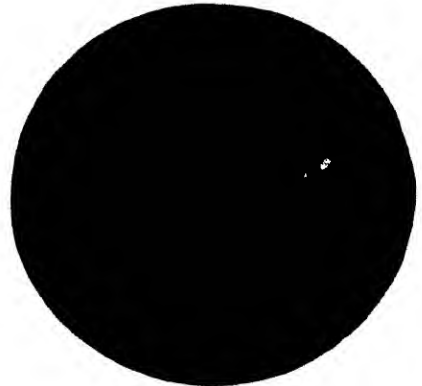
FIG. 20.

TABLE III.—THE RELATIONSHIP OF THE CONSTANTS C AND A.

Salt.	k.	s.	k/s.	$K \times 10^4$ (calculated).	$K \times 10^4$ (as given in the literature).
Copper ($C = 17.965$. Mean value of $A = 1.60 \times 10^{-2}$ neglecting bracketed terms. The bracketed term is 10.5×10^{-4}).					
CuSO$_4$ . .	79.5	3.58	22.2	232	—
Cu(OH)$_2$ . .	48.8	3.37	14.5	152	—
CuSO$_4$. 5 aq. .	124.9	2.27	55	577	458
Iron (Expt. 1.—$C = 23.417$. Mean value of A : 2.06×10^{-2}. Mean bracketed term, 6.29×10^{-4}).					
(Expt. 2.—$C = 10.920$. Mean value of A : 1.95×10^{-2}.					
Fe(OH)$_2$ . .	—	3.6 (corresponding to the specific weight of ferrous hydroxide)			
Fe(OH)$_2$ . .	44.9	(3.6)	12.5	78.6	—
FeSO$_4$ . .	76	2.99	25.4	160	—
FeSO$_4$. 7 aq. .	139	1.9	73.2	461	470

In the case of iron the conductivity of the solution present in the pores could be proved to be practically identical with that of a solution of common ferrous sulphate heptahydrate. By photographing it through a reflecting polarisation microscope the layer could actually be proved to be ferrous sulphate heptahydrate.

The following typical photographs (Figs. 5 to 9) show the covering of an iron electrode by anodic passivation with the strongly optically refractive ferrous sulphate.

Ohm's law was utilised in the following form in deducing equations 1 to 3:—

$$ e = E - (\epsilon_k - \epsilon_{me}) = i\left[w_0 + \frac{\delta}{\kappa(F_0 - F)} \right] \qquad . \qquad . \quad (4) $$

In this equation regard is given to the additional resistance which arises from the deposition of a primary surface F_0 on the total surface F by a layer of thickness δ, corresponding to κ the specific conductivity of the electrolyte in the pores. The product of this resistance with the current density, i, prevailing at any given moment, corresponds to the potential at which the electrode at that moment is nobler than the underlying metal. This polarisation of an electrode was formerly quite commonly considered to be due to an alteration of the potential of the metal itself. The validity of equation 1, in which the potential of the metal itself appears as a constant, shows that this value of the polarisation $\left\{ i \cdot \dfrac{\delta}{\kappa(F_0 - F)} \right\}$ is brought about solely by the resistance in the pores. This kind of polarisation, which was first known in the case of iron, we designate "layer polarisation."

In view of what has been said above, it was to be expected that passivation would arise with comparatively small current strengths when using a shielded electrode and that there must be a relationship between the strength of the current used at the commencement and the time which is necessary for passivation. The attainment of passivity is indicated by a sudden drop in the current strength.

Moreover, we may expect that the passivating period will be so much the longer as the initial current density is the smaller. In our equation 1 the passivating period is given as

$$ t_s = C = \frac{s\delta}{k(1 - u)} \frac{F_0}{i_0} = \kappa\delta\frac{F_0}{i_0} \qquad . \qquad . \qquad . \quad (5) $$

Systematic experiments on the relationship of initial current strength and passivating period showed, within extraordinarily wide limits, the validity of a simple law. If we represent the passivating period and the initial current strength on a double logarithmic co-ordinate system we obtain a straight line corresponding to the form of the relationship,

$$t_p = B\left(\frac{i_0}{F_0}\right)^{-n} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (6)$$

Fig. 10 shows some curves for the passivation of different metals.
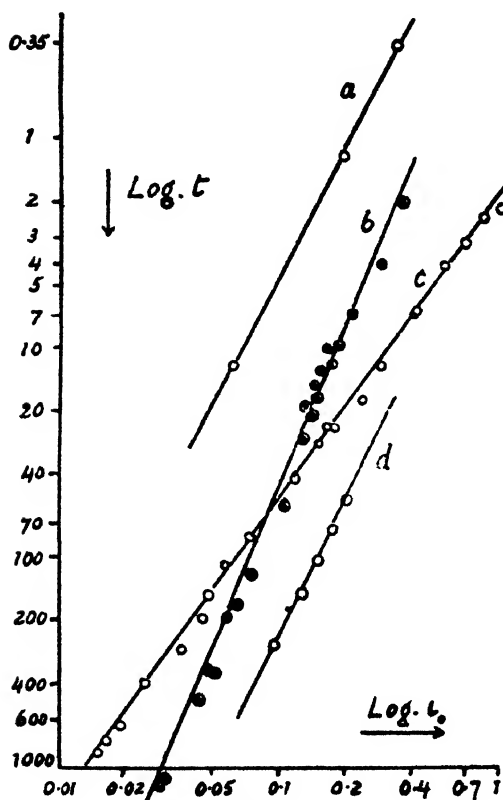
FIG. 10.

Fig. 11 shows the validity of this relationship in the case of iron in normal sulphuric acid when the initial current strength is varied a thousandfold and the passivating time is varied a hundred thousand-fold within the scope of the relationship.

If we compare equation 6 with the formula for the constant C, we see equation 6 arises if we put the thickness of the layer δ inversely proportional to a value of the current density. This proportionality coincides with a well-known observation in regard to crystallisation of substances from supersaturated solutions, viz., that the crystal size of the deposited material is so much the smaller as the solution is the more strongly supersaturated. The supersaturation existing at the limiting surface is, however, directly proportional to the current strength. If now we write

$$\delta = a\left(\frac{i_0}{F_0}\right)^{-m} \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

we arrive (by including this in the equation for C) at the experimentally found relationship. It is of interest that this equation holds good even if the electrolyte is not saturated with the salt in question. This at one time apparently puzzling fact can be explained if we consider that the saturation of the surface layer is very quickly brought about by quite a small migration of the heavy metal ions.

The effect of convection on a hanging electrode (or on an electrode in a stirred electrolyte is very readily proved by the aid of the i_0t relationship. In Fig. 12 the left-hand curve shows the i_0t relationship in the case of iron in normal sulphuric acid with a shielded electrode ; the middle curve gives
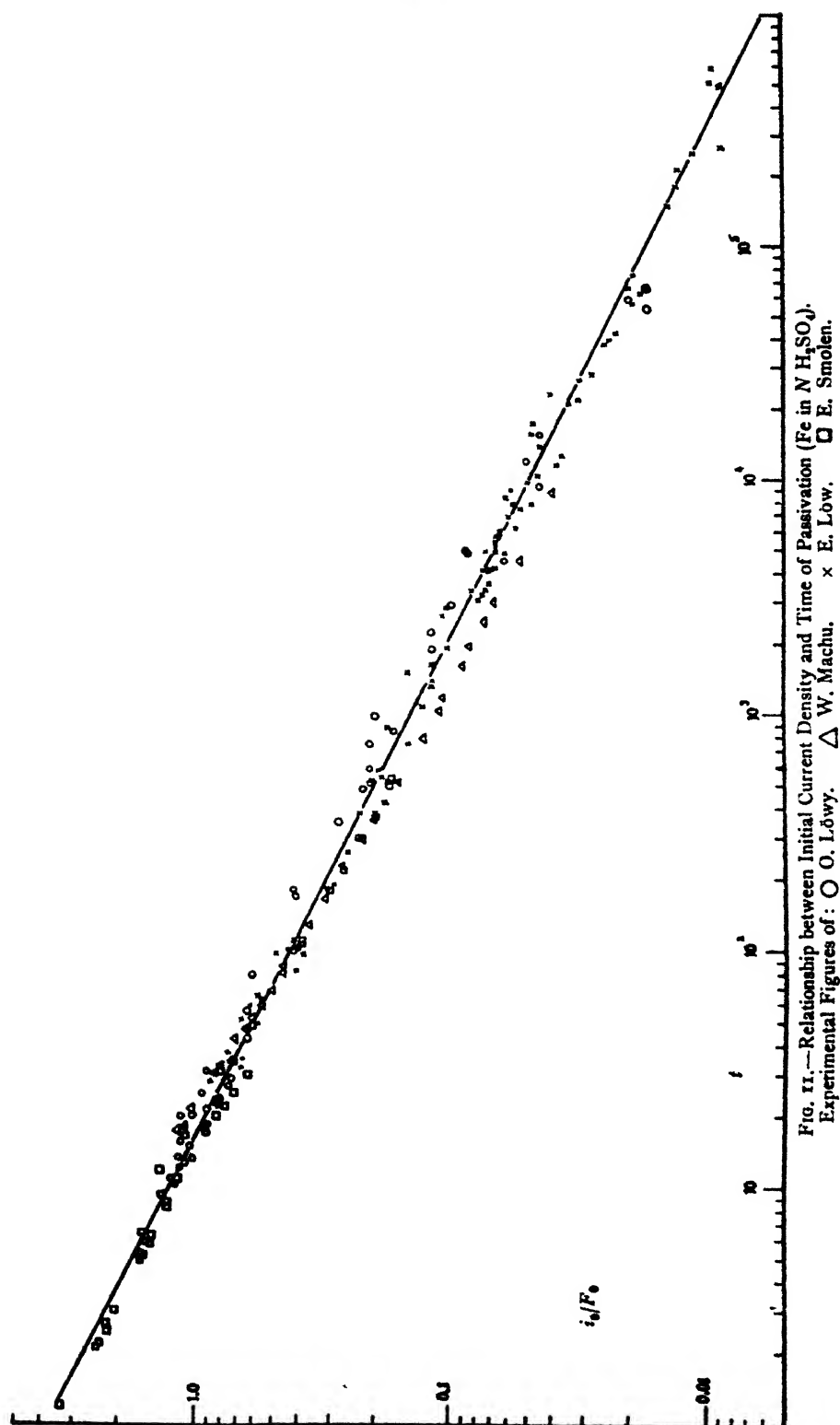
FIG. 11.—Relationship between Initial Current Density and Time of Passivation (Fe in N H_2SO_4).
Experimental Figures of : ○ O. Löwy.　△ W. Machu.　× E. Löw.　□ E. Smolen.

a picture of the values with the ordinary hanging electrode; the curve on the extreme right shows what happens if the electrolyte of the hanging electrode experiment is stirred. Since the iron salt is removed by convection from the surface layer in both the last-mentioned cases, the passivating period is correspondingly lengthened for equal initial current strengths. Moreover, we observe here that there is an initial current strength below which the metal no longer becomes passive, and that this is higher in the stirred than in the unstirred electrolyte. Only at quite high current densities do the values approach those for the shielded electrode; in such conditions the adhering layer, which cannot be detached even by stirring, becomes strongly supersaturated.

FIG. 12.

A further regularity which resulted was the following: if the process of rendering passive is so conducted that chemical passivity (*i.e.* change in the anodic process), cannot take place, the constant A in equation (1) rises sharply at the end. Hence we have another regularity in the development of the film. If we assume theoretically that, after reaching a definite potential value, there is no further growth on the surface, but that growth proceeds inwards, the following relationship is arrived at

$$t - t_0 = B\left(\frac{1}{i_1^2} - \frac{1}{i_0^2}\right) \qquad . \qquad . \qquad . \qquad (8)$$

where the constant possesses the value

$$B = \frac{\kappa E F_0^n s}{k(1 - u)} \qquad . \qquad . \qquad . \qquad (9)$$
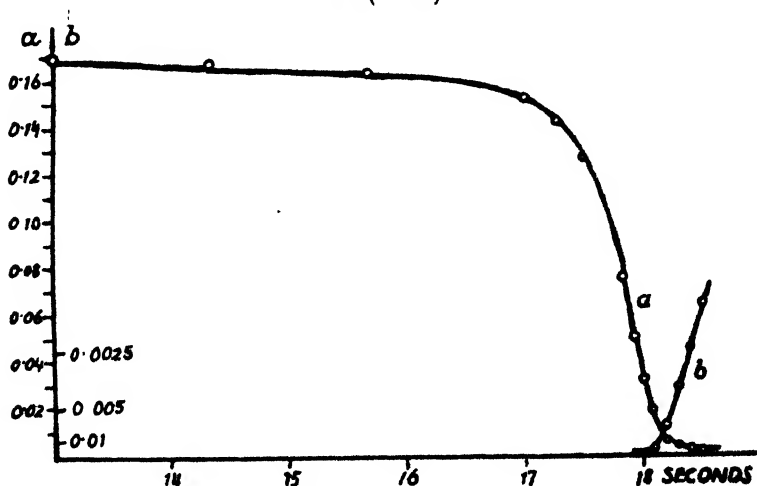
FIG. 13.—Copper.

The relation can be verified by plotting $1/i^2$ against time.   Figs. 13-16 show a series of examples of the validity of the equation.
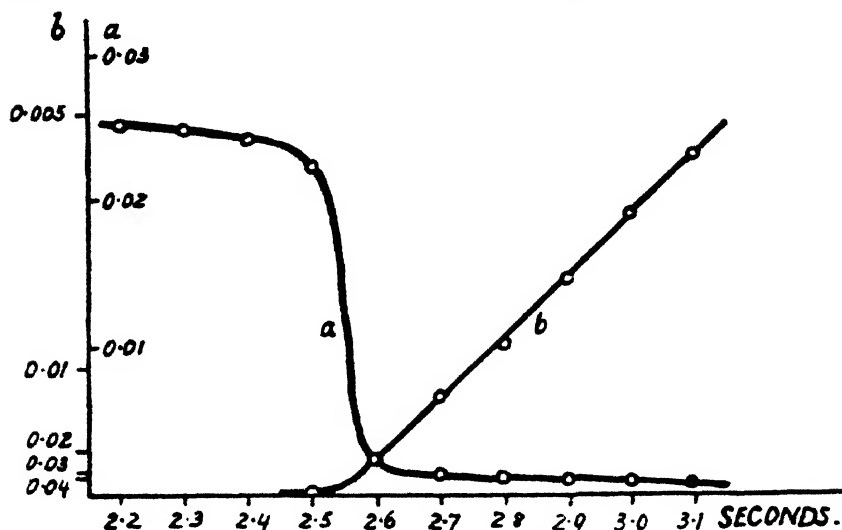
Fig. 14.—Lead, 1·5 volts.

So far it has held for all such cases considered.   It was especially interesting that in the cases of aluminium, chromium and other metals this relationship held for the beginning of the anodic treatment, whereby it was proved that these metals are covered extensively at the very beginning of their becoming passive with a layer of oxide containing only few pores. This explains at the same time (*e.g.* in the case of aluminium) the existence of high polarisation when no current is flowing.   In this case the polarisation can be explained by the action of local currents flowing from the metal through the pores towards the covering film.
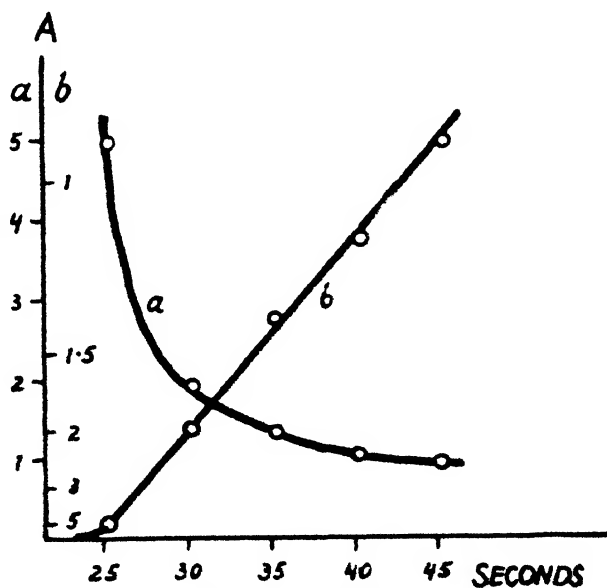
Fig. 15.—Aluminium.

The magnitude of this local current is derived from the potential difference between the metal and the film ($\epsilon_s - \epsilon_{ms}$) as well as the resistance in the pores $\left(w_p = \dfrac{\delta}{\kappa'(F_0 - F)} \right)$ and the resistance in the layer $\left(w_s = \dfrac{\delta}{\kappa F} \right)$,

where κ and κ' represent the specific conductivity of the film and of the electrolyte in the pores. The resulting back E.M.F., which we call "layer polarisation," is represented as E'. From this relationship we deduce the measured potential

$$e' = \epsilon_{m\rho} - (\epsilon_\rho - \epsilon_{m\rho})\frac{F\kappa'}{F\kappa' + \kappa(F_0 - F)} \qquad . \qquad . \quad (10)$$

The value $\dfrac{F\kappa' + \kappa(F_0 - F)}{F\kappa'}$ contains only the constants of the film and can be treated as a correction coefficient. If there is no film this value equals zero, and if the layer is complete the value equals unity; so that the measured potential can lie, according to the magnitude of the layer, between the potential of the metal and the potential of the covering film, the latter being regarded as the electrolyte potential at the unattackable film.
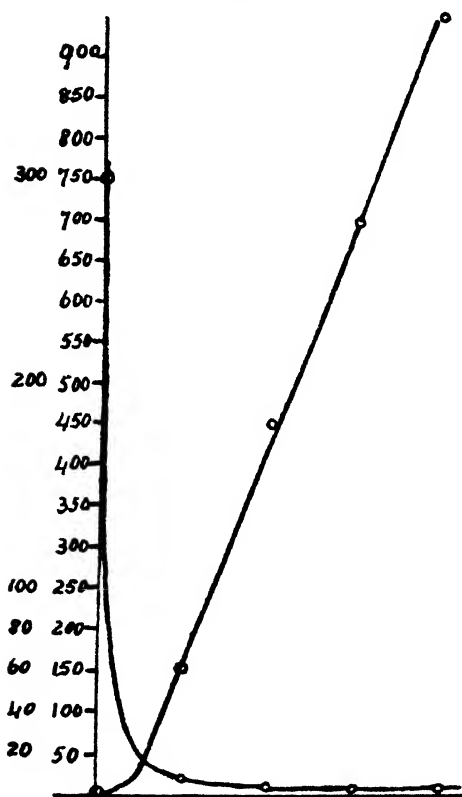
Out of this there results an electro-osmotic theory of the inhibition effect (*Sperreffekt*) for the valve action of aluminium anodes, according to which the change in the resistance is caused by the film being electro-osmotically compressed at the anode, thus forcing the electrolyte out of the pores, whilst at the cathode, where the film is stretched, it becomes thoroughly saturated with electrolyte, hence causing a much higher conductivity. By applying Kirchhoff's laws to a shielded electrode, the relations for the passage of a current through a shielded electrode can be represented as follows :—

Fig. 16.—Aluminium.

$$i_\rho = \frac{\kappa(F_0 - F)}{\kappa(F_0 - F) + \kappa'F}\left[(\epsilon_\rho - \epsilon_{m\rho})\frac{\kappa'F}{\delta} + i\right] \qquad . \qquad . \quad (11)$$

where i_ρ is the value of the current in the pores.

All these relationships gave possibilities for a systematic investigation of the anodic phenomenon of passivity under the most varied conditions and resulted in the following conclusions:—

(1) The metal that is used as an anode is not covered with a film, or the naturally existing film is soluble in the electrolyte. In this case the law of surface covering, equation (1) holds. The nature of the substance forming the covering follows from the constants, C and A, of the calculated conductivity of the electrolyte in the pores and when the substance is optically double refracting can be verified in the reflecting polarisation microscope.

(2) The metal is covered with an oxide film which is insoluble in the electrolyte. In this class the passivating time is in all cases considerably less than in class 1. In the case of a decrease in current strength the depth covering relationship holds, rather than the surface covering relationship.

(3) Chemical passivation (*i.e.* change in the anodic process), which consists either in the evolution of oxygen at the anode or in solution at a higher valency, can only take place when the current density in the pores exceeds such a definite critical value as causes a change of the underlying metal in the pores. If the ion entering into solution under these conditions at the anode is stable, and if the covering film remains unchanged, the metal goes into solution with higher valency (*e.g.* chromium, lead in concentrated sulphuric acid, thallium, iron in chloride solution, trivalent iron in bisulphite solution). If the film itself shows a considerable conductivity there occurs, in addition to solution at higher valencies, evolution of oxygen (*e.g.* iron and manganese in concentrated soda solution). If the higher valent ion entering into solution is not stable, but hydrolysed, under the conditions at the anode, then the layer of salts at lower valencies initially existing, changes into a layer of oxides of higher valency. Evolution of oxygen occurs in this secondary layer. To maintain chemical passivity of the first kind (solution at higher valency) the maintenance of high current density in the pores is necessary. In this state of the metal in the pores only, does it enter into solution with higher valency. If in the second case the conductivity of the film is somewhat higher, then, as has previously been said, the current density in the pores can sink so low that the metal enters into solution at lower valency, in spite of the evolution of oxygen which takes up a certain part of the energy of the current. This was observed particularly in the case of nickel.

The nature of the substances which form the primary covering depends first and foremost on the p_H of the electrolyte layer adjoining the anode, and the stability of the corresponding salt, but even this primary layer can show a change through hydrolysis. Thus iron which is freed from its oxide layer is covered primarily with iron sulphate heptahydrate in all sulphate solutions from sodium sulphate solutions to 10 N sulphuric acid. If passivity is brought about under conditions such that chemical passivity does not take place (*i.e.* when the effective potential is below 1·5 volts), the film of strongly double refracting ferrous sulphate heptahydrate can be changed in time to a basic salt which is no longer doubly refracting. This change takes place much more quickly with zinc and copper. In the case of nickel a non-polarised film of basic salt is obtained from the start provided that a not too concentrated (5-15 N) sulphuric acid is used. In concentrated acids there appears at first the normal doubly refracting salt, but this quickly changes into the non-doubly refracting basic salt. The explanation of this phenomenon lies, on the one hand, in the varied tendency of the metals to form complex salts (the more complex the structure of the metal the lower the p_H at which the basic salt appears), on the other hand, in the fact that a very small hydrogen ion concentration makes its appearance at the anode very quickly, owing to the great mobility of the hydrogen ion.

As has been stated, the passivating period can always be explained on the basis of the formation of a film. We can consider the constant B in the $i_0 t$ equation as the normal passivating time, corresponding to a current strength of one ampere. If we determine this constant B in sulphuric acid of different concentrations we get the values depicted in Fig. 17, which shows that at low concentrations ($N/10$) the values are very small. The value increases rapidly up to about $N/10$ and decreases slightly

with greater concentration of the acid. It can be shown that the decrease at higher concentrations is due to a proportionality between the solubility of the ferrous sulphate hepta-hydrate in the corresponding acid and the constant B. In sodium sulphate solution a fresh iron electrode has an extraordinarily short passivating period, which is obviously caused by the oxide film naturally formed on the iron in air. If, however, an electrode is alternately passivated several times in sodium sulphate solution and treated with acid, the passivating time after a while reaches approximately the value which is found in an equally concentrated sulphuric acid solution (see Fig. 17). In this case also we see the strong decrease when experiments are made with dilute solutions (o·1 N). In view of this state of things it seemed likely that in these very dilute solutions the super-oxidised covering film which, as has been stated above, is formed under the anodic influence of acid, exhibits a certain stability; on cathodic activation by contact with a zinc wire there would be a destruction of this film, whereupon an extension of the passivating time would be brought about. The result of this experiment was very remarkable. We obtained after a long activation of this kind in $N/10$ sulphuric acid a current-time curve of the form of Fig. 21. It differs completely from the normal deposition diagram.

FIG. 17.
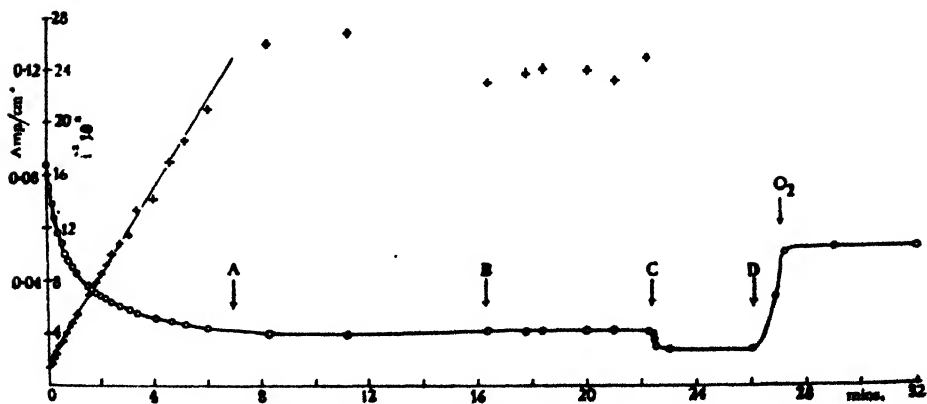
FIG. 21.—Fe; o·1 N H$_2$SO$_4$; 5·5 Volts; 1′ Zn.

As the indicated values of $1/i^2$ show, it depends strongly upon the proportional depth of the layer. The film arising in this case exhibits at first no double refraction, so that it consists either of a basic salt or hydroxide.

After some time the current strength increases somewhat and there is an alteration of the film which is visible to the naked eye; the film then begins to exhibit double refraction at various places, and this leads to a new decrease in the current which results from incipient chemical passivation under the influence of the acid. We are therefore led to conclude that in these dilute solutions the superoxide film (which is remarkably easily destroyed by activation with a zinc wire in more concentrated solutions) remains stable.

The spontaneous passivity of a metal which is active under certain circumstances is hence explained by the presence of a layer of oxide already formed in the air, as has been verified by Evans and others (in *Nature*) by dissolving away the metal. Such a film then tends only to make the metal passive if the size of the pores remains below a definite fraction of the whole surface, about 10^{-4} to 10^{-6}. The layer polarisation by a local current is then so great that the metal can no longer evolve hydrogen from acids (*e.g.* aluminium and passive chromium, etc.).

If the layer is destroyed (as happens for example with iron in most electrolytes which are not alkaline) the metal rusts, since when the pores increase the covering polarisation falls rapidly, the metal in the pores used as anode to the local current metal-electrolyte-film enters into solution. The metal which has gone into solution is oxidised by the solution to rust.
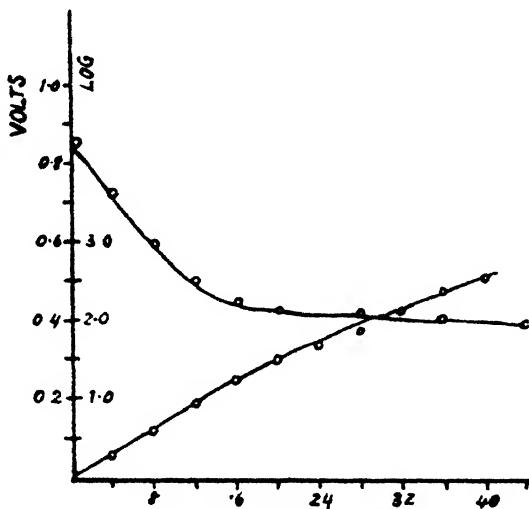
Fig. 22.—Al in H_2O.

Many metals show, in particular electrolytes, the phenomena of self-induced passivity where the potential rises to "inert" values. This phenomenon can be explained as covering by the local current going from the metal through the electrolyte to the covering film.

The theoretical calculation gave for the time period of the phenomenon the formula,

$$t = M\left(N + \frac{2.3}{\kappa} \log \frac{\epsilon_{m0} - \epsilon'}{\epsilon' - \epsilon_s}\right) \qquad . \qquad . \qquad . \quad (12)$$

the validity of which could be verified in a series of cases, especially in the case of aluminium chromium and some iron alloys.

The experiments also showed that the oxide theories (from Faraday to Haber), the metal change theory of Schönbein, especially the theory of the *Zwangszustand* of Hittorf and the author's explanation of them by the electronic theory, have their value, each within its limits. Furthermore the use of the new conception of layer polarisation allows of a quantitative formulation of the time relationships of the phenomenon of passivity, whereby a far-reaching classification of the process is possible in the most diverse cases.

Thus, in the case of iron, four different substances can be identified as forming the protective layer. The oxide film which is formed naturally on iron brings about almost instantaneous passivity in electrolytes, and especiallyin alkaline electrolytes, by anodic charging. If this film is destroyed or disturbed in acid electrolytes there results a film of ordinary ferrous sulphate heptahydrate, which changes at potentials in excess of about 2 volts to a film of a higher oxide of iron. This higher oxide film is apparently porous and only stable in very dilute solution. On extended activation in dilute solution and renewed passivation there arises a covering film of a basic salt.

The behaviour of nickel in sulphuric acid solutions is still more complicated, but an investigation of this would, however, lead us too far.

In the time at our disposal it has naturally not been possible in all cases to go into the ofttimes very laborious and detailed work which was entailed in the establishment, support and proof of the theoretical conceptions which have been mentioned. I desire, however, to take the opportunity of mentioning the names of my colleagues, Dr. Noack, Dr. Konopicky, Dr. Löwy, Dr. Holleck, Mr. Eltenton, Dr. Cameron and Dr. Machu without whose assistance this far-reaching work could not have been undertaken. Many problems in the sphere of the passivity of metals still remain unsolved. I hope, however, that a sufficient impression has been given to indicate that the knowledge already acquired in the field of passivity phenomena will act as a true guide in that labyrinth of which we speak as the passivity of metals.

Vienna, 27th August, 1931.

BIBLIOGRAPHY.

F. Foerster, *Elektrochem. wässriger Losungen*, Aufl. 23, p. 415, *et seq.*

W. J. Muller, *Z. Elektrochem.*, **30**, 401, 1924.

W. J. Müller, " Stromdichte-Spannungskurven," *Z. Elektrochem.*, **33**, 401, 1904.

W. J. Müller, " Stromdichte-Potentialkurven, besonders des Eisen," *Monatsch. Chem.*, **48**, 61, 1927.

W. J. Muller, " Passivität des Nickels," *Monatsh. Chem.*, **48**, 426, 1927.

W. J. Müller and E. Noack, " Pass. v. Chrom," *Monatsh. Chem.*, **48**, 528, 1927.

W. J. Müller and K. Konopicky, " Theorie der anodischen Polarisation," *Monatsh. Chem.*, **48**, 711, 1927.

W. J. Müler and K. Konopicky. " Stromdichte-Spannungskurve im Rest-Stromgebiet," *Z. Elektrochem.*, **34**, 12, 1928.

W. J. Muller and O. Lowy, " Stromdichte-Passivierungszeit," *Monatsh. Chem.*, **49**, 47, 1928.

W. J. Müller and K. Konopicky, " Stromdichte-Zeitkurve bei Bedeckungs-passivität," *Monatsh. Chem.*, **50**, 861, 1928.

W. J. Müller and O. Lowy, " Stromdichte-Passivierungszeit bei verschiedenen Elektrolyten, ' *Monatsh. Chem.*, **51**, 336, 1929.

W. J. Müller, " Einfluss von Deckschichten auf das Potential eines Metalles," *Monatsh. Chem.*, **52**, 53, 1929.

W. J. Müller and K. Konopicky, " Das anodische Verhalten des Aluminiums," *Z. physikal. Chem.*, **141**, 343, 1929.

W. J. Müller, " Kinetik der Passivitätserscheinungen," *Z Elektrochem.*, **35**, 656, 1929.

W. J. Müller and H. Holleck, " Passivität des Zinks," *Monatsh. Chem.*, **52**, 425, 1929.

W. J. Müller and H. Holleck, " Passivität des Kupfers," *Monatsh. Chem.*, **52**, 409, 1929.

W. J. Muller and K. Konopicky, " Zeitgesetz der Selbstpassivierung," *Monatsh. Chem.*, **52**, 463, 1929.

W. J. Müller and K. Konopicky, " Passivität des Bieins," *Monatsh. Chem.*, **52**, 442, 1929.

W. J. Müller and W. Machu, "Passivität des Eisens in Natriumsulfatlösungen,"
Monatsh. Chem., **52**, 474, 1929.

W. J. Müller and K. Konopicky, "Passivierung des Chroms," *Monatsh. Chem.*,
52, 289, 1929.

W. J. Müller and K. Konopicky, "Motoelektrische Effekt," *Monatsh. Chem.*, **53**,
and **54**, 707, 1929.

W. J. Müller and K. Konopicky, "Zur Theorie der Ventilelektrode," *Z. physikal.
Chem.*, A **145**, 241, 1929.

W. J. Müller, "Über Passivität von Metallen, Vortrag," *Sonderh. Korrosion und
Metallschutz*, p. 8, 1929.

A. Smits, "Passivität und Überspannung," *Z. Elektrochem.*, **36**, 20, 1930.

W. J. Müller, "Grundsätzliches zur theoretzichen Deutung der Passivität der
Metalle," *Z. Elektrochem.*, **36**, 6, 1930.

E. Müller and O. Essin, "Zur Passivität des Chroms I.," *Z. Elektrochem.*, 962, 1930.

W. J. Müller, "Discussion between Herrns A. Smits and the author," *Z. Elektrochem.*,
36, 8, 1930.

W. J. Müller, "Zur Theorie der Passivitätserscheinungen XII. Über den Strom-
durchgang durch Anoden, welche mit einer nicht loslichen Deckschicht bedeckt sind.,"
Monatsh. Chem., **139**, 461, 1930.

W. J. Müller, "Über die Theorie der Bedeckungspolarisation," *Z. Elektrochem.*,
36, 9, 1930.

W. J. Müller, "Zur Passivität des Chroms," *Z. Elektrochem.*, **37**, 6, 1931.

W. J. Müller and W. Machu, "Über die Natur der Deckschichten, welche bei
anodischer Pasi vierung von Eisen und sulfationenhaltigen Losungen auftreten, *Z.
physikal. Chem.*, "*Bodenstein-Festband*," 687, 1931.

THE CONSTITUTION OF AUSTENITE AND OF THE SOLID SOLUTION OF CARBON IN δ IRON AND OF THE LIQUID SOLUTION IN EQUILIBRIUM WITH THESE, EXAMINED THERMODYNAMICALLY.

By F. H. JEFFERY.

The following attempt to examine the molecular constitution of certain phases formed by the iron-carbon system is based on the determinations and diagrams of (i) Tschischewsky and Schulgin,[1] of (ii) Gutowsky,[2] and of (iii) Ruer and Klesper.[3] It will be found that these various diagrams are consistent and it has been assumed, therefore, that they are a fair representation of equilibrium conditions. For the calculations the atomic weights used are $Fe = 55.8$, $C = 12$.

(i) These authors determined the portion of the austenite boundary from the eutectoid point at $700°$ to the eutectic isothermal at $1130°$. They annealed ingots, etched them with chlorine, and rapidly chilled them, in vacuo. They concluded that this portion of the boundary was recti-linear, the points they used to determine it being 1.25 per cent. C. at $883°$ and 1.505 per cent. C. at $1010°$. They considered that the straight line joining the eutectoid point to the point 1.7 per cent. C. at $1130°$ approximated to the correct boundary. A straight line can be drawn from the 0.9 per cent. C. eutectoid point to pass between these two points and these are almost exactly on this line; this line meets the $1130°$ isothermal at 1.73 per cent. C. The calculations which follow have been made by using this line.

[1] Tschischewsky and Schulgin, *J. Iron and Steel Inst.*, **95**, 189, 1917.

[2] Gutowsky, *Metallurgie*, **22**, 731, 1909.

[3] Ruer and Klesper, *Ferrum*, **11**, 257, 1914.

Along this boundary the reaction taking place is austenite $\rightarrow$ cementite.

If austenite be a solid solution of monatomic molecules of carbon in monatomic molecules of iron, n being the molal fraction of carbon in the solvent iron

$$3Fe + C = Fe_3C,$$

$$\nu_0 \log (1 - n) + \nu \log n = \log K.$$

Where

$$\nu_0 = -3, \quad \nu_1 = -1,$$

$$-3 \log (1 - n) - \log n = \log K,$$

also

$$\frac{\partial}{\partial\theta} \log K = -\frac{\lambda}{R\theta^2},$$

giving

$$-3 \log (1 - n) - \log n = \frac{\lambda}{R\theta} + \left(\log K_{\theta_1} - \frac{\lambda}{R\theta_1} \right)$$

for sufficiently dilute solutions, where θ_1 is close to the superior limit of θ for which the equation is valid and λ is sensibly constant within the corresponding limit of concentration. Hence if the molecular constitutions have been correctly chosen $3 \log (1 - n) + \log n$ is a linear function of $\frac{1}{\theta}$. The results shown in the table were obtained.

θ.	Per Cent. Carbon in Austenite.	n.	$3 \log (1 - n) + \log n$.	$\frac{1}{\theta}$
1023	1·0	$4·49 \times 10^{-2}$	$\bar{2}·5920$	$9·775 \times 10^{-4}$
1076	1·1	4·92	$\bar{2}·6260$	9·294
1126	1·2	5·35	$\bar{2}·6564$	8·881
1179	1·3	5·77	$\bar{2}·6838$	8·482
1231	1·4	6·20	$\bar{2}·7087$	8·123
1283	1·5	6·61	$\bar{2}·7311$	7·794
1336	1·6	7·03	$\bar{2}·7519$	7·485

These points lie on the straight line through the second and the sixth. This leads to the conclusion that austenite is a solid solution of monatomic carbon in γ iron and not of Fe_3C in iron. Using the same concentrations of carbon calculations were also made on the assumption that this latter was true, the equation being

$$-\log n' = \frac{\lambda}{R\theta} + \left(\log K_{\theta_1'} - \frac{\lambda}{R\theta_1'} \right),$$

where n' is the molal concentration of Fe_3C in iron. The points obtained lay on a curve concave to the straight line joining the first and the last. Hence the simpler constitution of austenite follows from the boundary conditions.

(ii) This author determined the liquidus and solidus from the 1130° eutectic isothermal to 1480°. In spite of the fact that he did not use electrolytic iron his boundaries fit the appropriate points on Ruer's 1487° isothermal surprisingly well. If it be supposed that the liquid solution in equilibrium with austenite from 1130° to 1487° consists of monatomic molecules of carbon in monatomic molecules of iron and that austenite has the same simple constitution as found previously the corresponding thermodynamic equation is

$$-\log (1 - n) + \log (1 - n') = \log K$$

$$= \frac{\lambda}{R\theta} + \left(K_{\theta_2} - \frac{\lambda}{R\theta_2} \right),$$

where n and n' are the molal fractions of carbon in the liquid and solid phases respectively, θ_2 is in the neighbourhood of $1480°$ and λ is supposed to remain sensibly constant for the range of concentration used. The results shown in the table were obtained.

θ.	Per Cent. Carbon in Liquid.	Per Cent. Carbon in Solid.	n.	n'.	$-\log(1-n) + \log(1-n')$.	$\frac{1}{\theta}$.
1748	0·5	0·20	$2·28 \times 10^{-2}$	$0·92 \times 10^{-2}$	$0·601 \times 10^{-2}$	$5·721 \times 10^{-4}$
1723	0·8	0·25	3·61	1·15	1·095	5·804
1706	1·0	0·28	4·49	1·29	1·431	5·862
1681	1·3	0·33	5·77	1·52	1·916	5·949
1665	1·5	0·37	6·61	1·70	2·225	6·006
1648	1·7	0·40	7·44	1·83	2·556	6·068
1625	2·0	0·47	8·67	2·15	2·995	6·154

The points lie on a straight line joining the second and the fifth. This leads to the conclusion that the liquid phase consists of monatomic carbon molecules in monatomic iron molecules, and confirms the constitution of austenite previously obtained.

(iii) These authors determined the liquidus from their isothermal $1487°$ to the freezing-point of iron which they considered to be $1528°$, the transition point γ iron $\rightleftarrows$ δ iron at $1402°$, the boundary of the solid solution of carbon in δ iron from this point to the freezing-point, and also the austenite boundary from $1402°$ to $1487°$ which they took to be rectilinear. They used electrolytic iron and made their measurements with the metal in nitrogen.
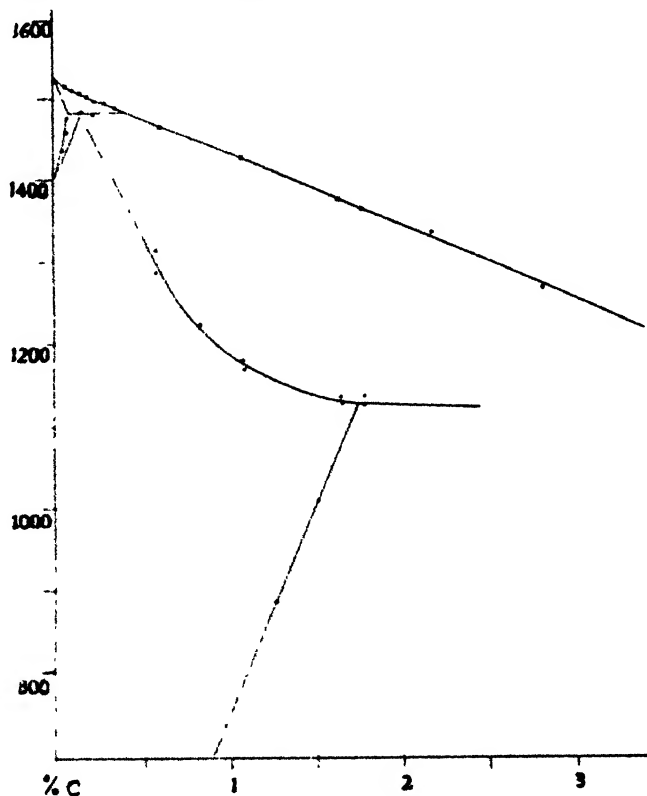
FIG. 1.

Calculations were made using their solidus and liquidus from $1487°$ to the freezing-point of iron. It is to be noted that they considered that a straight line was a sufficiently accurate representation of this portion of the solidus. The liquid phase was again taken to be monatomic carbon

molecules in monatomic iron molecules as there seemed no reason to assume any discontinuity of constitution at the temperature 1487°. The solid solution in δ iron was taken to be monatomic carbon molecules in monatomic iron molecules. The corresponding thermodynamic equation is

$$- \log (1 - n) + \log (1 - n') = \frac{\lambda}{R\theta} - \frac{\lambda}{R\theta_0}$$

where $\theta_0 = 1801$ the freezing-point, and λ is assumed to have the value for pure iron at θ_0, and not to vary sensibly for the range of concentration considered. The results shown in the table were obtained.

θ.	Per Cent. Carbon in Liquid.	Per Cent. Carbon in Solid.	n.	n'.	$- \log (1 - n) + \log (1 - n')$.	$\frac{1}{\theta}$
1801	0·00	0·00	0 × 10⁻³	0 × 10⁻³	0 × 10⁻³	5·552 × 10⁻⁴
1791	0·05	0·018	2·32	0·83	0·65	5·584
1787	0·10	0·026	4·63	1·20	1·48	5·596
1783	0·15	0·034	6·94	1·57	2·31	5·608
1775	0·20	0·048	9·23	2·23	3·05	5·634
1770	0·25	0·058	11·52	2·69	3·85	5·650
1767	0·30	0·063	13·80	2·93	4·78	5·659

The four middle points lie fairly well on a straight line through the first; the second and the seventh are somewhat further from it. This leads to the conclusion that the solid solution in δ iron also consists of monatomic carbon molecules in monatomic iron molecules and confirms the constitution of the liquid solution already found. Calculations were also made, using the same carbon concentrations, on the assumption that the solid solution in δ iron might consist of Fe_3C dissolved in monatomic molecules of iron. The results were altogether at variance with the boundary conditions.

In order to obtain further evidence as to the constitution of this solid solution the two-phase system represented between the two boundaries from the 1402° point for pure iron to the 1487° isothermal was examined. The constitutions of this solid solution and of austenite were taken as found previously. It seemed that the boundary conditions might be satisfied if, on cooling, carbon passed from this solid solution to the austenite and iron from the austenite to this solid solution simultaneously.

$$\nu_0 \log (1 - n) + \nu \log n + \nu_0' \log (1 - n') + \nu' \log n' = \log K,$$

where n is the molal fraction of carbon in the solid solution from δ iron and n' the molal fraction of carbon in austenite:

also $\qquad \nu_0 = 1, \quad \nu = -1, \quad \nu_0' = -1, \quad \nu' = 1.$
Hence

$$\log (1 - n) - \log n - \log (1 - n') + \log n' = \log K = \frac{\lambda}{R\theta} + \left(K_{\theta_2} - \frac{\lambda}{R\theta_2} \right),$$

θ_2 being in the neighbourhood of 1480°, and the corresponding value of λ being used for these dilute solutions. The results shown in the table were obtained.

θ.	Per Cent. Carbon in δ Solution.	Per Cent. Carbon in Austenite.	n.	n'.	$\log (1 - n) - \log n$ $- \log (1 - n')$ $+ \log n'$.	$\dfrac{1}{\theta}$
1751	0·07	0·16	$3·25 \times 10^{-2}$	$7·40 \times 10^{-2}$	$3·592 \times 10^{-1}$	$5·711 \times 10^{-4}$
1743	0·065	0·145	3·02	6·69	3·470	5·737
1735	0·06	0·13	2·79	6·00	3·339	5·764
1729	0·055	0·117	2·55	5·36	3·238	5·784
1723	0·05	0·105	2·32	4·85	3·212	5·804
1717	0·045	0·092	2·08	4·27	3·162	5·824
1711	0·04	0·08	1·85	3·71	3·030	5·844

These points lie on the straight line through the first and the last. This result confirms the results previously obtained for the constitutions of the two solid solutions.

Discussion of these Results.

1. All the parts of the diagram which involve austenite lead to the result that it consists of monatomic molecules of carbon dissolved in monatomic molecules of γ iron. The assumption that it is a solid solution of Fe_3C is incompatible with the boundary conditions as derived from the work of the authors quoted.

2. The liquid solution in equilibrium with the solid solution derived from δ iron and with austenite appears to consist of monatomic carbon molecules dissolved in monatomic iron molecules: here also there is no evidence of a compound of iron and carbon in solution.

3. Cesàro [4] using the determinations of Carpenter and Keeling concluded that both the liquid solution and austenite were derived from Fe_3C, the solvent being diatomic molecules of iron. It is to be noted that he used a thermodynamic equation applicable only to the case where the solid which crystallises from the liquid solution is the pure solvent.

4. The solid solution derived from δ iron also appears to be of simple constitution consisting of monatomic molecules of carbon dissolved in monatomic molecules of δ iron.

5. For both solid solutions the thermodynamic equations involve monatomic solvent molecules of iron and monatomic solute molecules of carbon, this should give rise to a simpler crystal structure of the solid solutions than if the solute molecules were those of a compound. It is known that γ iron has a face-centred cubic lattice and that austenite has the same type of lattice.[5]

[4] Cesàro, *J. Iron and Steel Inst.*, **99**, 447, 1919.
[5] Westgren, *J. Iron and Steel Inst.*, **1**, 303, 1921.

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THE FRACTIONATION OF NITROCELLULOSE BY MEANS OF AQUEOUS ACETONE.

By James Craik and F. D. Miles.

In this paper, it is proposed to give an account of a method for the fractional solution of a soluble nitrocellulose such that the number and amount of the fractions can readily be controlled, and to discuss some of the results obtained by its means (Part I.). It will be pointed out (in Part II.) that the successful conduct of this and of the allied method of precipitation depends on a knowledge of the solvation of nitrocellulose in solution, and of the absorption of the solvent by it when undissolved. The characteristic property of the nitrocotton on which such a separation depends will be discussed and certain means of characterising a nitrocellulose, or any elementary fraction of one, will be considered.

Many workers have fractionated industrial nitrocellulose and have examined the chemical and physical properties of the several components. Precipitation from solution, diffusion and filtration through membranes, have all been employed. Since the procedure to be described is closely related to that of fractional precipitation, it will be advisable to review briefly some of the more important accounts of separation by precipitation, before describing the development of fractional solution.

Review of Previous Work on Fractionation of Nitrocellulose.

Duclaux and Wollman[1] described some experiments on the fractional precipitation of collodion nitrocellulose from acetone solutions : they dissolved the ester in acetone and, with vigorous stirring, added a large volume of aqueous acetone (about 60 per cent. by volume), which gave a first fraction of 38 per cent. of the original weight used. By adding 20 per cent. acetone, they obtained a second fraction (43 per cent.) and, finally, a third by addition of a very large excess of water. The recovery of the nitrocotton was 95·4 per cent. The fractions were very nearly identical in nitrogen content, but varied very considerably in viscosity.

In later work reported by Duclaux,[2] the same method was followed. The precipitation was carried out by adding acetone-water mixtures of gradually diminishing proportion of acetone. Three fractions at most were obtained. The first was a gel. Curves were given showing the viscosity of the various fractions in solution in methyl-ethyl-ketone. Other methods of separation were also discussed. The diffusion of nitrocellulose from a gel into surrounding solvent, and the process of ultra-filtration were both reported to give a fraction very free from foreign matter. It is interesting to note that Duclaux ascribed the possibility of fractionation to difference in the micellar size.

Clément and Rivière[3] carried out one experiment by the same method, precipitating from acetone solution by adding water. The three fractions

[1] *Bull. Soc. Chim. France,* **27**, 414, 1920.   [2] *Rev. gén. Colloides,* **7**, 241, 1929.
[3] *Chim. Industrie,* **11/1**, 581, 1924.

(75 per cent., 20 per cent. and 5 per cent. of the whole) showed a marked difference in viscosity, and of these the two smaller showed a fairly large loss in nitrogen. It may be added that neither the viscosities nor the nitrogen contents of these fractions showed a proper balance with those of the original nitrocotton.

In a more recent communication, Beck, Clément and Rivière,[4] described an apparatus for the continuous fractionational precipitation of nitrocellulose by evaporation, under diminished pressure, of an aqueous acetone solution. By this means, fractions were obtained of almost the same nitrogen content. It was concluded, in agreement with Duclaux, that nitrocellulose is chemically homogeneous but physically heterogeneous.

Bréguet [5] applied the methods of Duclaux and Wollman to study the effect of heat and light on celluloids. He dissolved in acetone the material which had been exposed to light or heat, and used benzene as a precipitant to avoid co-precipitation of the camphor. He concluded that the deterioration of nitrocotton and celluloid was due to a gradual degradation of the highly polymerised nitrocellulose aggregates.

The separation of each of a number of industrial nitrocelluloses into fractions was carried out by Kumichel,[6] who also used the precipitation method. This worker recognised that the proportion of water which had to be added to an acetone solution to initiate precipitation varied from one nitrocotton to another. The point at which sufficient water had been added was shown by a sharp drop in the viscosity of the solution. He found, however, that neither of his two fractions was an individual substance, each appearing to contain some of the other, and on this account he abstained from systematic successive precipitations by the addition of increasing amounts of water, contenting himself with the division into two fractions by adding aqueous acetone (1 : 1) sufficient to give rise to " unmistakable external signs of incipient precipitation " (loc. cit.,[6] 169). As Kumichel himself pointed out, the amount of water required to give this result is dependent on the rate at which the addition is made, and on other factors.

PART I.

Methods and Results of Fractional Extraction.

Materials.—The nitrated materials were samples of industrial nitro-celluloses comprising as wide a range as possible of such properties as nitrogen content and viscosity. Details of these are given in Table I. The acetone gave no residue on evaporation; its density at 20° was 0·7910, and the various aqueous solutions were made up from this with distilled water. All percentages of acetone were accurately determined from the densities, and are given throughout this paper by weight.*

Experimental.

By repeating some of the experiments of Duclaux and other workers, it was soon established that although the nitrocotton could be separated into, say, three fractions, there were definite objections to the method on the

[4] *Chim. Ind.*, **24**, 1068, 1930.
[5] *Rev. gén. Colloid.*, **3**, 200-206, 230-235, 1925.
[6] *Kolloidchem. Beiheft*, **26**, 161, 1928.
* Determinations of the densities of aqueous acetone over the whole range of mixture had been made elsewhere in these laboratories. It is hoped to publish this series later.

ground that it was not possible to get a complete recovery of the nitro-cotton. There was usually a loss of about 5 per cent. A similar loss was also evident in Duclaux's experiments.[1]

Another type of experiment was open to the same objection. It had been observed from time to time in this laboratory that if water were added, drop by drop, to a clear acetone solution of nitrocotton, until the solution just showed signs of turbidity, three layers seemed to separate out after long standing. Isolation of these three layers by precipitation with water was carried out only with difficulty, and did not give a complete recovery of the nitrocotton.

Fractional precipation gives very little choice in the size and number of the fractions. A review of earlier results shows that the first fraction was invariably large, about 50 to 75 per cent. of the total weight of nitrocotton, and that it was unusual and extremely difficult to obtain more than three fractions. Experiments on these lines were therefore abandoned.

In preliminary trials of the solution method, the nitrocotton was divided into two fractions by shaking with aqueous acetone (20 c.c. to 1 gram). The residue was treated in the same way, a more concentrated acetone being used. The dissolved material was recovered by evaporation *in vacuo*. A complete recovery of the original weight of the product was possible in this way. With more experience the method was somewhat improved. It had the advantage that (1) any number of fractions could be isolated in a clean condition ; (2) a complete recovery of the nitrocotton was possible ; and (3) by varying very slightly the concentration of acetone it was easy to vary the size of the fractions.

This technique outlined above had certain disadvantages, the chief of which was that successive extractions of the same sample of material were involved, so that, except in the case of the first extraction, the extract and residue were not dependent solely on the composition of the solvent used for separating them. It was therefore decided to extract separate fresh amounts of nitrocotton with each concentration of acetone. The following method of extraction was finally adopted.

20 grams of nitrocotton, dried for 16 hours at 60° C., and 400 c.c. of the appropriate acetone, were shaken in a tightly stoppered wide-mouthed bottle on a horizontal shaker for two hours. The bottle was then placed (immersed to the neck) in a thermostat at 20° C., or any desired tempera-ture, and allowed to settle for 24 hours, or for longer in the case of a highly " kiered " material such as No. 3, or of one of very high viscosity such as No. 6. Provided the supernatant liquid was clear after this period, it was decanted or siphoned off into a tared round-bottomed flask. The residue was treated in an exactly similar manner with three additional quantities (400 c.c. each) of the same acetone, and the combined washings were collected in the flask. The final residue was drowned in a large quantity of water, filtered, dried and weighed. To isolate the extracted material, the acetone and water were removed under diminished pressure at a temperature not exceeding 30° C. until the solid matter remaining was constant in weight.

Results Obtained from Various Nitrocelluloses.

The final method outlined above was used to fractionate various types of nitrocellulose for which the essential data are recorded in Table I. All the samples, with the exception of Nos. 6 and 7, had been manufactured from cotton linters by a mechanical process of nitration. Attention is drawn to the viscosities of the solution in acetone, in the last column of

the table.   Excepting Nos. 6, 7 and 8, each of the materials had been *kiered*, *i.e.* treated with water under pressure to adjust its viscosity to a desired figure.   No. 4 for instance had been kiered for five hours under 20 lbs. pressure, and Nos. 1 and 3, as can be inferred from the table, had undergone more drastic treatment.

TABLE 1.

No.	Nitrogen. Per Cent.	Acidity as H_2SO_4.	Heat Test. Mins.	Bergmann and Junk Test. Mgm. N_2/gm. N/C.	Viscosity of 0·5 Per Cent. Solution in 99·6 Per Cent. Acetone at 20°.
1	10·33	0·076	12 12	0·65 0·60	0·00504
2	10·90	0·065	—	—	0·00941
3	12·01	0·041	11 11	0·75	0·00542
4	11·56	0·012	31 33	0·70 0·65	0·00793
5	11·53	0·016	—	0·85 0·80	0·00916
6	11·93	—	—	—	0·0496
7	12·04	—	23 23	0·81 0·77	0·0151
8	13·45	—	14 15	1·25	0·01413

Usually four to five points were determined, and the fractions (extracts and residues) so obtained were investigated for nitrogen content and viscosity.   In a few cases, stability tests were carried out.

FIG. 1
EXTRACTION CURVES OF VARIOUS CELLULOSE NITRATES.
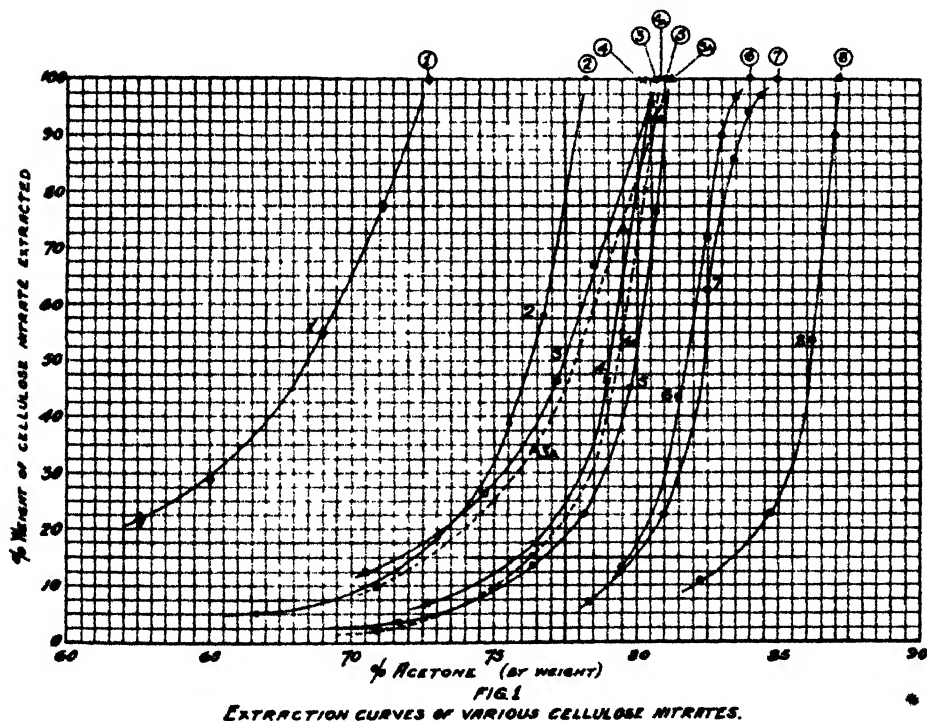
The weights of extracted material obtained by the use of various concentrations of acetone for the eight samples are given in Table II.

Two of the extractions were carried out at 15° C., the others at 20° C. ; the differences, due to temperature, seen in the data of Table II. and in the graphs of the results in Fig. 1 (curves 3A and 4A) show the necessity

TABLE II.—DATA FROM FRACTIONAL EXTRACTION OF NITRATED CELLULOSES.
(The figures in brackets in column 1 refer to curves in Fig. 1.)

Nitrated Cellulose.	Extraction Temp. °C.	Fraction.	Acetone Per Cent. by Weight.	Product Extracted Per Cent. by Weight.
1	20	A	62·54	22·0
		B	65 03	29·2
(1)		C	68·99	54·8
		D	71·09	77·2
2	20	A	66·64	5·2
		B	73·02	18·5
(2)		C	75·44	39·0
		D	76·78	58·0
3	20	A	70·54	12·5
		B	74·61	26·5
(3)		C	77·28	46·5
		D	78·51	67·2
3	15	A	70·93	10·0
		B	76·36	34·5
(3A)		C	79·47	73·0
		D	80·64	93·5
4	20	A	72·67	7·2
		B	76·57	17·7
(4)		C	79·00	46·0
		D	80·57	96·0
4	15	A	70·93	2·0
		B	76·36	15·0
(4A)		C	79·47	55·0
		D	80·64	93·0
5	20	A	71·65	3·5
		B	76·36	13·0
(5)		C	78·19	22·5
		D	79·73	42·5
		E	80·75	76·0
6	20	A	79·61	12·8
		B	81·56	43·2
(6)		C	82·54	71·2
		D	83·01	90·0
		E	83·51	97·2
7	20	A	78·39	6·8
		B	81·07	23·6
(7)		C	82·58	63·2
		D	83·44	86·0
		E	84·05	94·0
		F	84·89	97·2
8	20	A	82·36	10·5
		B	84·01	23·2
(8)		C	86·32	54·0
		D	87·06	90·0

of thermostatic control. The curves show interesting differences in gradient and in position. They have a fairly steep slope throughout the greater part of the extraction range, and it is apparent that the larger part of any nitrocotton tends to dissolve within a narrow critical range of acetone

concentration. In the case of No. 4 for instance, a rise of 2·5 per cent. in the percentage of acetone is sufficient to cause 70 per cent. of the nitro-cotton to go into solution. The gradient of the upper parts of the curves is roughly the same, but Nos. 1 and 3 are exceptional. These nitrocottons, as indicated in Table I., are the two of which the viscosities have been depressed, by treating with water under pressure, to figures lower than are shown by any of the others. Some interest attaches to Nos. 6 and 7, which, instead of having straight upper portions, turn slightly outwards and have on the whole an S shape.

Properties of Extracts and Residues.

Nitrogen Content.—In the early stages of this work, some difficulty was experienced in obtaining a good balance of nitrogen between the different fractions. It was soon established, however, that the fractions, and more especially the extracts, many of which were in a hard and horny state, were not in a suitable condition for estimation of nitrogen by either of the usual nitrometer or saponification methods.

Some work done at this time in the Analytical Section of these labora-tories showed that it was possible to regenerate such a dense nitrocotton in a very finely divided form suitable for nitrogen estimation by the nitro-meter. The solution in acetone was made slightly acid with hydrochloric acid, and water was then added from a fine jet, the solution being vigor-ously stirred. The extracts and residues in these experiments were sub-jected to this treatment before estimation of the nitrogen, and a very good balance was obtained between the fractions, the average loss being 0·7 parts in 100 parts of nitrogen. Two typical examples of these nitrogen balances are given in Table III. From these it will be seen that the most soluble fractions have the lowest nitrogen contents, and that the residues after extraction of the more soluble nitrocotton show nitrogen percentages

TABLE III.—NITROGEN DETERMINATIONS AND VISCOSITIES OF EXTRACTS AND RESIDUES FROM TWO TYPICAL EXPERIMENTS.

R = Original sample regenerated by evaporation and precipitation.

No.	Acetone Per Cent. by Weight.	Extracts.			Residues.			Recovery	
		Nitrogen Per Cent.	Viscosity, 0·5 Per Cent. Solution.	Per Cent. Weight Ex-tracted.	Nitrogen Per Cent.	Viscosity, 0·5 Per Cent. Solution.	Per Cent. Weight of Residue.	of Nitro-Cotton Per Cent.	of Nitrogen Per Cent., Corrected for Loss of Material.
4	—	11·56	0·007929	—	11·56	0·007929	—	—	—
R	—	11·50	0·007718	—	11·50	0·007718	—	—	—
A	72·67	9·52	0·00509	7·2	11·70	0·00777	92·8	100·0	100·4
B	76·57	10·86	0·00542	17·7	11·68	0·00816	82·3	100·0	99·9
C	79·00	11·42	0·00630	46·0	11·56	0·00920	50·0	96·0	99·1
D	80·57	11·49	0·00750	96·0	11·56	0·01890	2·0	98·0	99·5
7	—	12·04	0·0151	—	12·04	0·0151	—	—	—
A	78·39	10·22	0·00568	6·8	12·12	0·0169	93·2	100·0	99·6
B	81·07	11·04	0·00711	23·6	12·20	0·0208	76·0	99·6	99·7
C	82·58	11·89	0·0107	63·2	12·40	0·0305	36·0	99·2	99·7
D	83·44	12·08	0·0140	86·0	12·34	0·0252	13·2	99·2	100·7
E	84·05	12·11	0·0149	94·0	12·29	0·0242	4·4	98·4	100·7
F	84·89	11·94	0·0132	97·2	10·06	0·0230	2·4	99·6	98·7

slightly higher than the original substance. Although such differences as 9·52 per cent. and 11·70 per cent. are seen in this table, the first extract and the last residue are very small, and, as more equality is reached between extracts and residues, there is rarely a greater difference in nitrogen than 0·3 to 0·4 per cent. The comparative constancy of composition of the fractions which has been found by previous workers is confirmed.

Viscosities of Fractions.—Viscosity determinations were carried out by the Ostwald-Poiseuille method at 20° (0·5 gm. per 100 c.c. of acetone). It should first be noted that there is a slight difference in viscosity between the original nitrocotton and one which has been regenerated from solution either by evaporation, precipitation, or by the combined operation. To take Sample 4, for instance, it was found that its viscosity was 0·007929 c.g.s., which value fell to 0·007828 after precipitation from acetone, and to 0·007718 after a combined process of evaporation followed by precipitation. Similar results were obtained with other samples. McBain and his collaborators [7] found that a nitrocotton recovered from acetone solution by precipitation with water had a higher viscosity than the original material. No evidence of such an increase was obtained. Even a small loss of the material of very low viscosity will raise that of the precipitate very considerably. Such a loss is not unlikely to occur, for it is evident from the figures given that the material of lowest viscosity is the last to be precipitated.

It was found, as might be expected, that the viscosities of the residues are higher and those of the extracts lower than that of the original nitrocotton. The variation from one extract or residue to another of the same nitrocotton is still under investigation and is not completely understood. The typical case, to which all others approximate more or less closely, is that of No. 4. It is evident from the figures of Table III. that as the amount of residue is diminished its mean viscosity continuously rises. If the viscosity of a mixture of nitrocelluloses may be regarded as an additive property, this must mean that as extraction is carried out with acetone of increasing strength the additional dissolved fractions possess a progressively rising viscosity. In some cases, however, as in that of the residues of No. 7, there seems to be some disturbing factor which prevents this process from being uniform over the whole range.

Stability.—Kumichel (*loc. cit.*,[6] p. 189) gave the results of stability tests on the fractions of one nitrocotton containing 11·5 per cent. of nitrogen. The more soluble fraction, corresponding to the "extract" of this communication, he found was quite unstable, but the less soluble portion (our "residue") was more stable than the original material.

Some of the fractions isolated in the course of this work were examined by the Heat Test and the Bergmann and Junk test, but the results did not lead to very definite conclusions. The behaviour of fractions Nos. 8A and 8B (Table II.) was what might be expected from Kumichel's work, but in all other cases both extracts and residues were less stable than the original materials, and, in addition, the extracts sometimes showed a higher stability than the residues. It was found, however, that the process of solution in and regeneration from acetone was itself responsible for a decrease in the stability of the nitrocotton. Sample 4 for instance gave a result by both the heat test (15 mins.) and by the Bergmann and Junk test (2·40 mgms. N_2 per gm.) which was lower than that given (32 mins.; 0·70, 0·65 mgms.) by the original material. A sample of No. 8 behaved in the same way

when examined by the heat test (before treatment 15 mins. ; after $3\frac{1}{2}$ mins.). The suggestion which has often been made, that when a nitrocotton loses its fibrous structure the stability can no longer be estimated in the usual way, is supported by these results.

Other Properties.—With the exception of the extracts which comprised less than 15 per cent. of the whole, the fractions were all white in appearance. The physical state of a fraction depends partly on the type of nitrocotton and partly on the method of precipitation. A high nitrogen product like No. 8 can be precipitated in the form of a soft powder, but a heavily kiered product (No. 3) will cause more difficulty in regeneration and give a horny product. The most soluble fractions (extracts representing 15 per cent. or less) were slightly yellow or brown in colour, were fairly brittle when precipitated, and could very readily be ground to a fine powder.

PART II.

The Dependence of Fractionation and Precipitation on Solvation and Absorption of Acetone.

To conduct successfully a fractionation of nitrocotton by extraction with a mixed solvent required some knowledge of the physico-chemical relations between the nitrocotton and the solvent constituent of the mixture. If, for instance, nitrocotton is immersed in an acetone-water mixture containing too little acetone to dissolve it, acetone is absorbed, and the acetone concentration of the liquid phase is reduced. If the mixture is of higher concentration, and nitrocotton is dissolved in it, the absorption of acetone still occurs—in the form of solvation—and the reduction of the acetone/water ratio in the free solvent can be demonstrated by various physicochemical means. Work on the solvation of nitrocotton has been carried out in these laboratories for some time. The results may be communicated later. For the present, it will be assumed that the solvation in aqueous acetone, the composition of which lies within a few per cent. of that of the mixture in which the nitrocotton becomes insoluble, is 1·1 gram of acetone to 1 gram of nitrocotton. This value has been found to remain much the same from one nitrocotton to another, and over a moderate range of concentration of dissolved material. It will be seen later that the observations on the precipitation from aqueous acetone are alone sufficient to yield a solvation value which agrees well with that already given and obtained by quite different methods.

Experiments on the absorption of acetone from mixtures containing less of this constituent than is necessary to dissolve the solid have also been made, and have shown that the absorption rises with the proportion of acetone, and, when the nitrocotton is just on the point of dissolving, becomes very nearly equal to the amount solvated when solution has just taken place.

It is possible in the case of either absorption or of solvation that the portion of solvent which is attached to the solid or to the solute is not wholly acetone, but may contain water as well, and that the total amount may be considerably greater than 1·1 gram (to 1 gram of solute). The apparent solvation, which alone can readily be determined, is the amount of pure acetone which is attached, when no account is taken of a possible further quantity of adhering solvent having the composition of the liquid as a whole. In the present connection, however, only the apparent solvation is significant.

It is then apparent that in experiments of the precipitation type the effective acetone concentration of a nitrocotton solution in pure acetone, to which water has been added to cause precipitation, cannot be calculated solely from the total amounts of acetone and water, but must be dependent also on the amount of nitrocotton present. The critical concentration of acetone at which precipitation occurs cannot therefore be found unless the solvation data are given, although it may be approximated if the precipitation is conducted in very dilute solution, so that the composition of the free solvent is only slightly affected by solvation. If 5·0 gm. of a nitrocellulose, the solvation of which is 1·00 gm. per gram, is dissolved in 100 gm. of aqueous acetone of 90 per cent. by weight, the free solvent contains, instead of 90, 89·5 per cent. of acetone. If, however, only 0·5 gm. were dissolved, the percentage of acetone in the free solvent would be reduced only to 89·95 per cent.

In a similar way, if an extraction were carried out in one operation by agitating the nitrocotton with an aqueous acetone of known initial composition, the effective acetone/water ratio to be correlated with the extraction observed would be unknown, but would be in all cases lower than the initial ratio on account of both absorption and solvation. By repeating the extraction, however, with separate quantities of the same solvent, these difficulties are avoided, for the solvent last used contains little if any dissolved matter, and the undissolved material has reached absorption equilibrium in the previous washing. A given degree of extraction, therefore, can always be correlated with the composition of the acetone in use when the extraction is complete.

The Critical Acetone/Water Ratio.

It is clear from the form of the curves of Fig. 1, and from the fact that none of them becomes quite vertical to the axis of acetone concentration, that precipitation of nitrocellulose, as the proportion of water increases continuously, must be perfectly continuous if sufficient time is allowed for equilibrium to be maintained. In other words, the nitrocellulose may be considered to consist of a series of elements, each requiring for solution aqueous acetone of definite composition, the necessary ratio of acetone to water being for any element slightly lower than for the element next to be dissolved. This critical acetone/water ratio is evidently a characteristic property of each element of the material, on which the fractionation by either extraction or precipitation alone depends.

In the characterisation of nitrocelluloses, the determination of "compatibility point" is frequently made. To a solution of the material in pure acetone, water is added until a slight addition produces incipient precipitation. The volume of water added to 100 c.c. of the solution is taken as a measure of the compatibility of the nitrocellulose with water in acetone solution. The results of such tests, having reference only to the least compatible fractions, should correspond only to the points in Fig. 1 at which the curves meet the upper horizontal bounding line representing 100 per cent. extraction. That the "compatibility points," determined by a method to be mentioned later, do actually coincide in most cases with the terminations of the extraction curves may be seen from the figure, these points (Table VI.) being indicated by numbered circles on the margin of Fig. 1.

To ascertain the influence of concentration on this determination, experiments were carried out on nitrocotton No. 4 at room temperature, by dissolving a known weight in 100 c.c. of acetone (99·75 per cent. by

weight).   Water was added drop by drop from a burette, the solution being shaken after each addition.   The end point was usually quite sharp.   By varying the concentration from 1·0 to 10 per cent., the figures in the first three columns of Table IV. were obtained.

TABLE IV.—COMPATIBILITY POINTS—NO. 4 NITROCOTTON AT ROOM TEMPERATURE.

Weight of Nitrocellulose in 100 c.c. of 99·75 Per Cent. Acetone (d = 0·792).	Volume of Water Added.	Per Cent. Acetone (by Weight) in Total Solvent.	Per Cent. Acetone (by Weight) in Solvent, Corrected for Solvation.
1·0 gm.	19·20	80·3	80·2
	19·20		—
3·0 ,,	18·85	80·5	80·0
	18·95		—
3·3 ,,	18·70	80·7	80·1
5·0 ,,	18·13	81·2	80·2
10·0 ,,	16·6	82·5	80·4

These preliminary results show that the concentration of acetone in the total solvent at the precipitation point rises with the amount of nitrocellulose present.   In the fourth column is given the critical composition of the solvent on the assumption that for every gram of nitrocotton 1·1 gram of pure acetone is removed by solvation.   The critical solution concentration thus calculated is nearly constant.   To obtain results independent of solvation it is clearly necessary to work with dilute solutions.

The influence of temperature in changing the degree of extraction has already been noticed.   The "compatibility point" of Nitrocotton No. 4 was determined as before, but only 0·5 gm. was dissolved in 100 c.c. of acetone, and the experiment was carried out in a thermostat at various definite temperatures.   The results are given in Table V.

TABLE V.—CRITICAL SOLUTION CONCENTRATIONS FOR NO. 4 NITROCOTTON (EXTRACTED) AT VARIOUS TEMPERATURES.

Temperatures.	Volume of Water Added to 100 c.c. Acetone (99·75) Per Cent.) Containing 0·50 gm. N/C.	Per Cent. Acetone (by Weight) in Total Solvent.
0° C.	17·0	82·3
20° C.	19·1	80·5
40° C.	21·4	78·7
60° C.	23·8	76·9

The very small correction for solvation has been omitted.   The increase of the dissolving power with temperature is most marked.

By the same method, but at constant temperature only, the critical solution concentration was determined for the nitrocottons of Table I., and also for several others (L, M, N).   These results, together with the nitrogen percentages, are given in Table VI.

There is a marked tendency for the critical solution concentration to rise with the percentage of nitrogen, but the effect is complicated by other factors.   In these tests, only the most insoluble fraction is considered. If different fractions of the same nitrocotton are taken, it is clear from the data given in Table III. that there must be a connection between the critical concentration and the viscosity.

TABLE VI.—CRITICAL SOLUTION CONCENTRATIONS OF CERTAIN NITROCOTTONS, DETERMINED AT 20°.

No.	Per Cent. Nitrogen.	C.S.C. for 0·5 Per Cent. Solution (°/₀ Acetone).	No.	Per Cent. Nitrogen.	C.S.C. for 0·5 Per Cent. Solution (°/₀ Acetone).
1	10·33	72·7	7	12·04	85·0
2	10·90	78·3	L	12·33	82·2
5	11·53	81·0	M	12·65	84·1
4	11·56	80·3	N	13·08	85·6
6	11·93	84·0	8	13·45	87·2
3	12·01	80·8			

The Determination of Solvation from Critical Solution Data.

It has been found possible to derive from critical solution data a value for the solvation of nitrocellulose which agrees fairly well with that determined in other ways. For this purpose, a method was employed which was more accurate than the "compatibility point" determination, and depended on the fact that the addition of nitrocellulose to an acetone solution of slightly higher than critical solution concentration is followed first of all by solution, and then, owing to the solvation of the dissolved material lowering the effective concentration of acetone, the critical solution concentration is reached and no further material can dissolve. If the solvation remains constant throughout this interval, it can be calculated from the data. In this way, in the range of 0·5 to 5·0 gm. of nitrocellulose to 100 c.c. of acetone, the solvation per gram of acetone at 20° was found for four different nitrocottons, the nitrogen content of which lay between 11·4 and 11·7 per cent., to be 1·2, 1·2, 1·2 and 1·3 grams of acetone.

To a pure solvent such as acetone, nitrocellulose can be added as if the two substances were liquids miscible in all proportions. In the case of a mixed solvent, in which one of the constituents has no solvent properties, there is an important difference. In aqueous acetone, the solvation must always impose a limit to the amount of dissolved material.

On the evidence which has been given, we regard every nitrocellulose as a mixture not of a limited number of components as has frequently been suggested, but of a continuously varying series of almost constant chemical composition, showing, however, from any one to the next, an appreciable difference in critical concentration of acetone necessary for solution. It is apparent that the distribution of viscosities is of the same kind. The method of fractional solution is well adapted for the further examination of this problem.

Most previous workers have ascribed these differences in the properties of nitrocellulose fractions to variation in micellar size, but their explanation does not lead very far. Recent information regarding the solution properties of substances consisting of long molecules of high molecular weight make it more probable that the dispersed nitrocellulose exists in solution as single chains of nitrated hexose residues,[8] and that the viscosity is greater the longer the chain. In any solution which is not very dilute, these chains will be in contact at various points, the forces uniting them at these points being of the same nature as those which maintain the molecules in contact in the fibre. A solvent such as acetone, which has affinity for the active groups in the residue, can break these linkings, partly by increasing the

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[8] See e.g. Staudinger, Z. physikal. Chem., 153, 391, 1931.

average distance between chains, but mainly by combining with the molecule at some or all of its active points. A nitrocellulose will be dissolved when its original intermolecular bonds have been broken to such an extent that each molecule can have independent motion. In aqueous acetone, the concentration at which there is sufficient active acetone to produce this separation will be the critical solution concentration.

Summary.

(1) A method is described for the fractionation of nitrocellulose by solution in aqueous acetone. The principal advantages of this method are that the number and size of the fractions can easily be controlled and that both extracts and residues are readily recoverable.

(2) The results with eight technical nitrocottons are shown in the form of tables and curves. The curves show significant differences in slope and position. From a nitrocotton which has received special treatment to reduce its viscosity, less can be dissolved within a given range of acetone concentration than from an untreated one.

(3) The nitrogen contents of fractions and of the original sample may be balanced if appropriate analytical methods are used. Residues have a nitrogen content slightly higher than the original substance ; small end fractions may be exceptional.

(4) Certain other properties are discussed. Progressive extraction of a nitrocotton tends to remove material of continuously increasing viscosity.

(5) The dependence of fractional solution or precipitation on the solvation of dissolved nitrocotton by acetone, or on adsorption of acetone by undissolved nitrocotton, is pointed out. A value for the solvation is given.

(6) A nitrocellulose may be separated into a series of elements each of which requires for solution aqueous acetone of definite critical concentration, the necessary acetone water ratio being, for any element, slightly lower than for the next element to be dissolved.

(7) The determination of critical solution concentration is discussed. On account of solvation the results vary in a calculable manner with the concentration of nitrocellulose. They also vary with temperature. The critical solution concentration rises with the nitrogen content and for any element of a nitrocotton rises with the viscosity.

THE HEAT TREATMENT OF THE γ-MONO-HYDRATE OF FERRIC OXIDE.

By R. D. Williams, M.Sc.,* and J. Thewlis, M.Sc.,†

Introduction and Previous Work.

It is a long established fact that many ignited metallic oxides alter in properties considerably according to their method of preparation and treatment. The behaviour of ferric oxide is very striking in this respect. A

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large amount of previous work in this field has been carried out with a view to establishing the existence of a magnetic form of ferric oxide. It was first noted by Robbins[1] that there existed a form of ferric oxide different from that already known in that it was ferromagnetic. Similar observations were made later by Malaguti[2] and by Liversidge.[3]

More recent investigations may roughly be divided into two classes. On the one hand, the work has been based on the heat treatment of magnetite,[4] and, on the other, it has been based on the heat treatment of hydrated ferric oxide.[5] The second group has found that the magnetic form of ferric oxide is obtained by heating the γ-hydrate. Heating the α-hydrate produces the usual form of Fe_2O_3.

While the various workers have agreed that a magnetic form of ferric oxide exists at 350° C., and is converted to the normal ferric oxide in the region of 600° C. no range of oxides obtained by heat treatment at smaller temperature intervals appears to have been examined. Further, though the point of maximum activity has been roughly determined to be about 350° C., its cause and extent have not been satisfactorily determined. The activity has been attributed to a variety of factors such as particle size, surface conditions, nature of the crystal lattice, etc.

It therefore seemed desirable to make a systematic investigation of the crystal structure and activity of the γ-hydrate and the effect of heat treatment on these properties. Accordingly, precipitated hydrated ferric oxide was obtained in the γ-form (i.e., with the lepidocrocite structure), and heat treated over a temperature range of 200°-600° C. at intervals of 50° C., and also at 800° C. and 1000° C., the activity and crystal structure being determined at each stage.

The present paper is concerned with the changes in crystal structure brought about by the heat treatment of this monohydrate.

Experimental.

(a) Preparation of γ-Hydrate.

The γ-hydrate was prepared in another connection sometime previous to this work, from a dilute solution of ferrous chloride, by precipitation with calcium hydroxide in the form of a suspension in water and subsequent oxidation at room temperature   The product was washed by decantation with water at 50° C. until the filtrate indicated the absence of calcium and chloride ions, filtered and air dried at 30° C. for 40 hours. Analysis showed it to consist of a monohydrate containing 2·06 per cent. hygroscopic water.

(b) Method of Heat Treatment.

The heat treatment of the iron oxide hydrate was carried out in a high temperature furnace thermostatically controlled to maintain within ± 1° C.

[1] Chem. News, 1, 11, 1859.   [2] Ann. Chem. et Physique, ser. 3, 49, 214.
[3] Trans. Aust. Assoc., Hobart Meeting, 1892.
[4] Welo and Baudisch, Phil. Mag., 50, 399, 1925; J. Biol. Chem., 65, 215, 1925; Chem. Ztg., 49, 661, 1925; Naturwiss., 14, 1005, 1926; Phil. Mag. (7), 3, 396, 1927; Sosman and Posnjak, J. Wash. Acad. Sci., 15, 329, 1925; Chevallier, Compt. rend., 180, 1473, 1925; 184, 674, 1927; Abraham and Planiol, Compt. rend., 180, 1328, 1925.
[5] Hugget and Chaudron, Compt. rend., 186, 1617, 1928; Albrecht, Ber., 62B, 1475, 1929; Huttig and Zorner, Z. anorg. allgem. Chem., 184, 180, 1929; Huttig and Garside, Z. anorg. allgem. Chem., 179, 49, 1949; Simon and Schmidt, Kolloid Z., Spec. No. 65, April 1, 1925; S. Veil, Ann. Chim., 5, 135, 1926; Compt. rend., 184, 1171, 1927; Emmet and Love, J. physic. Chem., 34, 41, 1929.

FIG. 1.

any desired temperature between 200° and 1000° C. About 5 gm. of the hydrate were placed in a silica test tube, the latter transferred to the furnace, and the tip of a thermocouple embedded as near the centre of the material as possible. The temperature was then raised to 200° C., and maintained there for two hours. At the end of the period, the material was removed and stored in a sealed test tube. This procedure was repeated for temperatures of 250°, 300°, 350°, 400°, 450°, 500°, 550°, 600°, 800°, and 1000° C. At each stage in the heat treatment the material was analysed chemically and by X-rays.

(c) Method of Analysis.

(1) **Chemical Analysis.**—This included the estimation of combined and uncombined water and ferric oxide content. The uncombined water was determined by heating a known weight, about 1 gm. at 100° C. for one and a half hours and reweighing. On another portion the total water content was determined by introducing a weighed quantity of the material in a platinum boat into a silica combustion tube and the temperature of the latter was slowly raised to dull red heat. A current of pure dry air drawn through the tube swept the moisture evolved through tared absorption tubes containing calcium chloride. The tube was maintained at dull red heat for about half an hour before allowing to cool down. The absorption tubes were then reweighed, the increase in weight giving the total water content whence, by difference, the combined water. The iron oxide content was estimated by weighing out a further portion of about 0·5 gm. and treating with hot concentrated HCl until completely dissolved. A few drops of concentrated HNO_3 were added and the solution boiled to ensure complete oxidation of the iron. Ammonium chloride was then added followed by ammonia in slight excess. The precipitated iron oxide was allowed to settle and the supernatant liquid poured through a filter. After washing as far as possible by decantation the precipitate was wholly transferred to the filter and washed with hot water. It was then ignited and weighed as iron oxide.

(2) **X-ray Analysis.**—X-ray powder photographs were taken of the naturally occurring lepidocrocite, of the laboratory prepared hydrate and of the series obtained by heat-treating this hydrate. A circular camera was employed of 5 cm. radius, a Shearer X-ray tube being used with an iron target. The photographs obtained are reproduced in Fig. 1.

(d) Results.

The X-ray powder photographs of lepidocrocite and the laboratory prepared γ-hydrate were found to be almost identical (Fig. 1 "a" and "b"), the slight differences being probably due to the presence of impurities in the former since each line of the laboratory prepared γ-hydrate has an identically corresponding line on the lepidocrocite photograph.

On heating to 200° C. the water content had only decreased to 9·80 per cent. and the X-ray photograph again showed the lepidocrocite pattern (Fig. 1 "c").

At 250° C. the water content was 6·91 per cent. and new lines appeared on the X-ray photograph in addition to the lepidocrocite pattern which still persisted (Fig. 1 "d").

At 300° C. the water content was 4·40 per cent. The lepidocrocite pattern had disappeared entirely from the X-ray photograph and its place was taken by the new one, which appeared at 250° C. This pattern is very like that of Fe_3O_4 and is due to the formation of ferromagnetic Fe_2O_3

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(Fig. 1 "e"), the chemical analysis indicating that only Fe_2O_3 was present in the material.

Investigation of the effect of heating to 350°, 400°, and 450° C. showed that no change had taken place in the crystal structure of the material (Fig. 1, "f," "g," "h") and chemical analysis showed that the oxide was still Fe_2O_3 and that it was practically completely dehydrated at 350° C.

The specimen which had been heated at 500° C. still exhibited the pattern of cubic Fe_2O_3 but the presence of new lines due to the formation of α-Fe_2O_3 (rhombohedral structure) could be detected (Fig. 1, "j").

At 550° C. the material gave an X-ray photograph showing the α-Fe_2O_3 pattern principally, but the γ-Fe_2O_3 pattern still persisted (Fig. 1, "k").

The X-ray photographs of the specimens heated at 600°, 800°, and 1000° C. were all alike (Fig. 1, "m," "n"), and showed only the α-Fe_2O_3 pattern.

(e) Particle Size.

It will be noticed that the lines of the cubic Fe_2O_3 are broader than either those of the hydrate or the rhombohedral Fe_2O_3. This is due to the small size of the crystals of cubic Fe_2O_3. The lines, being due to diffraction, lose sharpness when the number of regularly spaced diffracting planes in the crystal falls below a certain amount. A parallel effect occurs with ordinary light. An optical grating which possesses only a few lines has a low resolving power, in other words, the diffraction maxima lose their sharpness. In the case of X-ray diffraction, loss of sharpness begins to occur when the crystals are about 10^{-5} cm. across. Any further diminution in size is accompanied by a corresponding increase in the breadth of the lines. This breadth, in fact, is a measure of the size of the crystalline particles. The connection between the breadth of X-ray lines and particle size has been investigated by several workers, and a concise account is given by Wood in a paper on the grain size in steels.[6]

The particle sizes in the present investigation were estimated by assuming Laue's equations,[7] and Brill's correction.[8] The half-breadth used in the equation (i.e., the breadth of a line at half its maximum intensity), was found by obtaining a photometer record and making the measurement thereon. A Moll self-recording micro-photometer was used.

The results were found to be as follows :—

The γ-hydrate particles are of the order of 10^{-5} cm. The particles of cubic Fe_2O_3, when they first appear (i.e., at 250° C.) are of the order of 5×10^{-7} cm. There is no change in size up to 300° C., but at 350° C. the particles of γ-Fe_2O_3 have begun to grow. They grow steadily until the temperature reaches 450° C. when they are of the order of 10^{-6} cm. Above this temperature, until the change over to α-Fe_2O_3 is complete, there is no further alteration in particle size. The particles of αFe_2O_3 are of the order of 10^{-4} cm. at 550° C., and further heating up to 1000° C. does not cause any change.

The foregoing results are briefly summarised in Table I.

Thus it will be seen that two changes in crystal structure occur on heating the γ-hydrate. Neither change is sudden, i.e., there does not appear to be a definite transformation temperature in either case. The first change (γ-hydrate to cubic oxide) begins about 250° C. and is complete at 300° C. The second change begins about 500° C. and is complete at 600° C.

[6] Phil. Mag., 10, 1073, 1930.

[7] Z. Krist., 64, 115, 1926.   [8] Ibid., 68, 387, 1928.

TABLE I.

Temperature of Heat Treatment.	Water Content.	Chemical Formula.	Crystal Structure.	Particle Size.
Prior to heat treatment	12·20 per cent.	$Fe_2O_3 . H_2O$	L	About 10^{-5} cm.
200° C.	9·8	—	L	About 10^{-5} cm.
250° C.	6·91	—	L + a small amount of C	L about 10^{-5} cm. C about 5×10^{-7} cm.
300° C.	4·40	—	C	About 5×10^{-7} cm
350° C.	1·60	—	C	
400° C.	—	Fe_2O_3	C	Crystals grow steadily
450° C.	—	Fe_2O_3	C	
500° C.	—	Fe_2O_3	C + a small amount of R	C about 10^{-6} cm. R not possible to estimate
550° C.	—	Fe_2O_3	R + a small amount of C	R about 10^{-4} cm.
600° C.	—	Fe_2O_3	R	About 10^{-4} cm.
800° C.	—	Fe_2O_3	R	About 10^{-4} cm.
1000° C.	—	Fe_2O_3	R	About 10^{-4} cm.

L = lepidocrocite structure.   C = cubic Fe_2O_3.   R = rhombohedral Fe_2O_3.

Summary.

$Fe_2O_3 . H_2O$, prepared from ferrous chloride by precipitation with calcium hydroxide and subsequent oxidation at room temperature, has the same crystal structure as the mineral lepidocrocite (the γ-hydrate). On heating it is converted first into the cubic form of Fe_2O_3 and later into the rhombohedral form. There is no definite transition temperature in either case. The first change takes place over a range from roughly 250° C. to 300° C., and the second over a range from roughly 500° C. to 600° C. The crystals of the γ-hydrate are of the order of 10^{-5} cm. across, and those of the α-oxide are of the order of 10^{-4} cm. across. When the crystals of the γ-oxide are first formed they are of the order of 10^{-7} cm. and gradually grow, their final size, i.e., just before transformation, being of the order of 10^{-6} cm.

AN EXPERIMENTAL INVESTIGATION CONCERNING THE PHOTOSYNTHESIS OF CARBOHYDRATES IN VITRO.

By James Bell.

The original experiments of Baly and his co-workers[1] on the reduction of carbon dioxide in aqueous solution to formaldehyde by illumination with ultra-violet light were subjected to considerable

[1] Baly, Heilbron and Barker, *J.C.S.*, 119, 1025, 1921.

criticism by Porter and Ramsperger,[2] Spoehr,[3] Bauer,[4] and others, who suggested that the formaldehyde owed its origin to traces of organic impurities. Applying Warburg's view [5] that photosynthesis *in vivo* is a surface reaction, Baly later [6] illuminated aqueous suspensions of powders on which carbon dioxide was strongly adsorbed. Under these conditions he claimed that the product of the photosynthesis consisted of carbohydrate compounds instead of formaldehyde.

A most interesting advance was described in 1927, when it was stated [7] that, by the use of visibly coloured powders, such as nickel and cobalt carbonates, the photosynthesis could be effected by means of visible light. The reaction now approximated more closely to that occurring in the living plant, and it appeared probable that further investigations might lead to the elucidation of the problem of carbon assimilation and the photosynthesis of carbohydrates *in vivo*.

Experiments on similar lines have been described by Mezzadroli [8] and by Dhar.[9]

The work now described was undertaken in the hope that, by the application of more exact methods than those hitherto employed, information concerning the mechanism and energetics of the reaction would be obtained.

In a recent publication [10] Baly claimed that very satisfactory yields of carbohydrates could be obtained using a catalyst consisting of ferric oxide supported on kieselguhr which had been previously coated with alumina. Increased activity of the catalyst was obtained by the addition of small quantities of thorium dioxide to the ferric oxide. Such supported ferric oxide catalysts of varying composition have been used in the present work.

Experiments were carried out using sources of illumination of widely varying intensities; the duration of illumination was also varied. In all cases, the amount of alumina in the aluminated kieselguhr was 22 per cent., but catalysts were prepared with ferric oxide contents of 1, 4·7, 10, 14· and 26 per cent., the ferric oxide always containing 0·64 per cent. of thorium dioxide. No evidence of photosynthesis was obtained using any of these catalysts, although cataphoresis measurements showed that these powders, when in suspension in an aqueous solution of carbon dioxide, assumed an electropositive charge. The carrying of such a charge has been claimed as an indication of a photosynthetically active catalyst.

As a support for catalysts in work of this type, kieselguhr is unsatisfactory on account of the large calcium content. Complete removal of the calcium is difficult, and where mineral acid is employed for this purpose, the removal of the last traces of acid from the kieselguhr presents a further difficulty.

After the failure of these experiments with supported ferric oxide

[2] Porter and Ramsperger, *J.A.C.S.*, **47**, 79, 1925.
[3] Spoehr, *J.A.C.S.*, **45**, 1184, 1923.
[4] Baur and Rebmann, *Helv. Chim. Acta*, **5**, 828, 1922; Baur and Büchi, *ibid.*, **6**, 959, 1923.
[5] Warburg, *Biochem. Z.*, **166**, 386, 1925.
[6] Baly, Davies, Johnson and Shanassy, *Proc. Roy. Soc.*, **116** A, 197, 1927.
[7] Baly, Stephen and Hood, *ibid.*, **116** A, 212, 1927.
[8] Mezzadroli and Gardano, *Atti Accad. Lincei* [6], **6**, 160, 1927.
[9] Dhar and Sanyal, *J. physic. Chem.*, **29**, 926, 1925; Gopala Rao and Dhar, *ibid.*, **35**, 1418, 1931.
[10] Baly, *Nature*, **126**, 666, 1930. *Trans. Far. Soc.*, **27**, 545, 1931. Discussion on Photosynthesis.

catalysts, the original work in which nickel carbonate was used as catalyst was re-examined. Electrolytically prepared nickel carbonate,[11] activated as described, was used. The experimental conditions outlined by Baly were followed as closely as his description allowed, but the results were determined by estimation of organic carbon in the residues obtained after illumination and subsequent evaporation. The method of estimation (described in experimental section) was a " wet " oxidation method, and tests showed that it was capable of detecting quantities of carbon, present as carbohydrate, as small as 1 mg.

The results indicated quite definitely that no photosynthesis of organic matter had taken place.

Experimental.

As the carbon dioxide supplied in cylinders is often obtained from the fermentation industry and therefore constitutes a possible source of organic impurity, all experiments were performed using carbon dioxide prepared from marble and hydrochloric acid. For purification the gas was passed first through a tube 12 ins. long containing copper oxide heated to redness, then through a bubbler containing chromic and sulphuric acids. After passing through a bubbler with distilled water, the gas passed into a tube 10 ins. long packed with solid sodium bicarbonate, and finally into another distilled water bubbler from which the gas entered the reaction vessel.

The reaction vessel used was a rectangular glass cell $14 \times 17 \times 7.5$ cm., open at the top, and having polished sides; a glass plate formed a convenient cover. The method of carrying out the photosynthesis tests was as follows. The required weight of the catalyst was suspended in $1\frac{1}{2}$ litres of specially distilled water in the reaction vessel and a fairly rapid stream of carbon dioxide (3 bubbles/sec.) was passed through the suspension. The gas was, as a rule, allowed to pass for half-an-hour to one hour before illumination of the vessel took place, and a steady stream was maintained throughout the period of illumination. After illumination, the catalyst suspension was allowed to settle. In some cases the suspension was more stable, and flocculation was assisted by warming to $60°-70°$. After filtration from the catalyst, the water was distilled off under reduced pressure, the aqueous distillate being tested for the presence of formaldehyde by means of Schryver's test. The residues appeared to consist largely of catalyst which filtration had failed to remove. In the earlier experiments, this residue was extracted with carefully purified absolute alcohol, but this procedure was later abandoned, owing to the difficulty of removing the last traces of the alcohol, apparently adsorbed on the catalyst. The traces of alcohol gave charring with concentrated sulphuric acid, and so led to erroneous results.

Kieselguhr-Supported Catalysts.

Before being used for the preparation of the catalyst, the kieselguhr was heated for seven to eight hours with a considerable excess of nitric acid (50 per cent.) to remove the calcium. The greater part of the acid was removed by washing by decantation; the kieselguhr was then transferred to a 12-in. Buchner funnel and washed with water until

[11] Baly and Hood, *Proc. Roy. Soc.*, 122 A, 393, 1929.

the washings were entirely free from acid, this operation generally occupying about four days.   The kieselguhr was then dried.

The method of preparing the supported ferric oxide catalysts was that adopted by Baly.

The coating of the kieselguhr with aluminium hydroxide was carried out by the addition of ammonium hydroxide to a suspension of kieselguhr in aluminium nitrate solution ; the resulting aluminated kieselguhr was washed with cold water, and after being thoroughly dried, was ignited at 450° to 480°.   It was then finely ground in a porcelain ball-mill, and coated with ferric oxide by evaporation with a solution of ferric nitrate as described by Baly.   Before the final ignition in a vacuum, the catalyst was once more ground in the ball-mill.   In all preparations, the ferric oxide contained 0·64 per cent. thorium dioxide, this being added in the form of the nitrate to the ferric nitrate solution.

Table I. gives examples of the catalysts used, the light sources, and the duration of illumination.

TABLE I.

Wt. Catalyst. g.	Fe_2O_3 %.	Light Source.	Distance from Cell. Ins.	Exposure Hours.
5	1	1000 c.p.	8	3·5
10	4·7 ⎫		9	7
20	4·7 ⎬	250 watt lamp	9	7
10	7·5 ⎭		9	7
4·5	10	1000 c.p.	8	5
20	14	250 watt lamp	12	6·5
46	14	60 ,, ,,	14	7
50	14	100 ,, ,,	24	8
		(½ voltage)		
7·5	26	1000 c.p.	8	3

No evidence was ever obtained that any photosynthesis had taken place.   Specific tests for carbohydrates, such as the Molisch reaction, gave negative results, and the residue (if completely free from alcohol) gave no charring with concentrated sulphuric acid.

The catalysts prepared exhibited an electropositive charge when suspended in a saturated aqueous solution of carbon dioxide, and while measurements were not obtained with a high degree of accuracy, the cataphoretic velocities were found to be of the order of 0·00025 to 0·00035 cm. per sec.   According to Baly [10] the most active powders show a velocity of 0·0004 cm. per sec.

Nickel Carbonate Catalyst.

The nickel carbonate was prepared electrolytically as described by Baly. [11]   Three nickel plates 20 × 7 × 0·3 cm. were suspended in a large cylindrical vessel containing distilled water saturated with carbon dioxide.   The plates were connected to a 220 volt circuit, in such a way that the two outer plates were made cathodes.   Two cooling coils, through which water was circulated, were suspended on either side of the central plate.   By means of a variable external resistance, the current was kept at 1 to 1·5 amp., and during the whole period of electrolysis a stream of pure carbon dioxide was passed through the solution.   The

nickel carbonate deposited at the negative plates, collected at the bottom of the cell, and was filtered off and dried at 100°. After being ground, it was heated at 130° to 140° for half an hour and once more very finely ground.

According to Baly and his collaborators,[7][11] the nickel carbonate must be subjected to a process of activation before use as a catalyst. This may be carried out by illumination with ordinary white light, or with ultraviolet light. The nickel carbonate used in the present work was always activated by one of these methods before being used.

(a) *By White Light.*—The finely ground nickel carbonate was spread in a thin layer on a large glass plate covered by a second plate to prevent contamination by dust. This was illuminated for seven hours by a 100 watt metal filament lamp placed immediately above the plate. The catalyst was always activated just before being used in a photosynthesis test.

(b) *By Ultra-violet Light.*—Nickel carbonate was spread in a thin layer on a glass plate and illuminated for three-quarters to one hour by the direct light of a mercury arc lamp placed about 9 ins. distant, the powder being stirred at intervals to expose fresh surfaces. The catalyst was used immediately after activation.

For the photosynthesis tests with nickel carbonate, the following method was used. The required weight of the catalyst was suspended in 1500 c.c. of distilled water and a fairly rapid stream of carbon dioxide passed in, while the cell was illuminated by the light of a 100 watt lamp at a distance of 9 ins. Illumination was continued for two to two and a half hours. At the end of that time the undissolved nickel carbonate was removed by filtration, and the green solution, containing nickel in the form of the bicarbonate, was evaporated to dryness under reduced pressure. The solution was filtered from precipitated nickel carbonate at intervals during the evaporation.

Estimation of organic carbon in the residue was carried out by the method developed by Mills,[12] a similar form of apparatus being used. The residue from the evaporation which always contained nickel carbonate was dissolved in 50 c.c. of very dilute sulphuric acid, and the solution transferred to the oxidation flask and warmed to 30° to 35° for twenty to thirty minutes, while it was evacuated by the water pump. Tests showed that this effectively removed carbon dioxide arising from inorganic carbonate.

A. R. concentrated sulphuric acid (100 c.c.) was added to the solution and the oxidation carried out with chromic acid (10 c.c.) as described by Mills. The absorption train for the carbon dioxide was on a much smaller scale, consisting of conical flasks of 50 c.c. capacity, and the total volume of baryta solution was 35 c.c. Instead of weighing the precipitated barium carbonate the excess baryta was determined by titration with standard acid, phenolphthalein being used as indicator. Blank experiments were carried out on the reagents, including the distilled water used in the photosynthesis experiments. The accuracy of the method was tested by dissolving weighed amounts of sucrose in 50 c.c. of the dilute sulphuric acid and treating this solution exactly as described. Table II. gives an example of the accuracy attainable.

Photosynthesis tests were carried out using approximately 5, 10, 30, and 50 g. of nickel carbonate in 1500 c.c. water. No visible evidence of

[12] Mills, *T. Soc. Chem. Ind.*, **50**, 375, 1931.

TABLE II.

Sucrose Added g.	N/10 HCl equiv. to CO₂ Formed c.c.	Carbon.	
		Found.	Theor.
0·0149	11·35	0·0062	0·0062
·0079	6·45	·0032	·0033
·0137	9·9	·0057	·0058

photosynthesised carbohydrate syrup was ever obtained, and tests for formaldehyde in the aqueous distillates gave negative results.

Blank experiments were carried out using nickel carbonate suspended in the same volume of water (1500 c.c.), and carbon dioxide passed through for the same length of time as in the photosynthesis tests, the reaction vessel being kept in darkness throughout this period.

The results of the carbon estimations in the residues from the blank experiments and from the photosynthesis tests are given in Table III.

TABLE III.

Experiment. Wt. Catalyst, g.	Total Organic Carbon Found. g.	Reagent Blank (mean).	Nett Organi Carbon. g.
Dark blank with NiCO₃	0·0016	0·0007₄	0·0008₈
	·0017₉	·0007₄	·0010₅
	·0014₂	·0007₄	·0006₈
Photosynthetic Tests.			
5	0·0018	0·0007₄	0·0010₆
10	·0015₅	·0007₄	·0008₁
30	·0014₈	·0007₄	·0007₄
50	·0014₂	·0007₄	·0006₈

The fact that there is no difference betweeen the amounts of carbon found in the dark blanks and the photosynthesis tests indicates that this carbon is due to impurity in the water, nickel carbonate, or the carbon dioxide used. It is quite possible that the whole of this carbon is contained in the distilled water used, as the value found represents an organic carbon content of less than one part per million.

The results indicate quite clearly that no conversion of the carbon dioxide to carbohydrate compounds had taken place.

Summary.

The work of Baly and his co-workers on the photosynthesis of carbohydrates in visible light has been repeated, but no evidence of such photosynthesis has been found, nor the production of any formaldehyde detected.

Ferric oxide photocatalysts, supported on kieselguhr, have been used, with negative results. The catalysts were found to bear an electropositive charge when in suspension in water saturated with carbon dioxide. According to Baly this is an indication of photosynthetic activity.

Nickel carbonate has also been employed as catalyst without success, the results of these experiments being determined by estimations of organic carbon in the residues.

In conclusion, I desire to thank Professor F. G. Donnan, F.R.S., for his continued interest and advice during the course of this investigation, and Mr. C. F. Goodeve for his criticism and suggestions. I wish also to record my gratitude to the Ramsay Memorial Trustees for the award of a Glasgow Fellowship.

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A THERMODYNAMIC STUDY OF THE IRON-CARBON SYSTEM IN THE SOLID AND LIQUID STATES (I.).

BY YAP, CHU-PHAY.[*]

Recently, Jeffrey in a series of articles [1] has shown the application of the thermodynamic laws of solution to metallic solid solutions. His treatment, however, does not appear to be as rigorous as that shown by the writer in the case of the iron-carbon system.[2] Because of the general interest and probable wide applications of the thermodynamic method to the study of metallic system, the writer believes it is not out of place here to discuss first the theoretical basis of the equations which we shall use in this paper, in order that we may always keep in mind the limitations of the thermodynamic method. Improperly applied, the method may cause considerable confusion, which may eventually discredit its use.

From the classical laws of the depression in the freezing-point of a solvent A, of molar concentration (mol-fraction) x_A, we have

$$\frac{d \ln x_A}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_A}{R} \qquad \qquad \qquad (1)$$

and it can be easily shown for a system showing solid solubility the following equation is applicable :

$$\frac{d \ln\left(\frac{x_L}{x_S}\right)_A}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_A}{R} \qquad \qquad (2)$$

In this case x_L/x_S is the ratio of the molar concentration of the solvent A in the liquid and solid states respectively and ΔH_A is the heat of fusion of

A per mol. In both equations above, if we plot $ln\ x_A$ and $ln(x_L/x_S)_A$ against $1/T$, the slope of the curve will give the molal heat of fusion of A. If the system is an *ideal solution*, and ΔH_A is constant, then the curve will be a straight line. Often even if the solution is ideal, still ΔH cannot be considered as constant ; hence, we have to provide for the change in the value of ΔH. If we let $T_A - T' = \theta$, where T_A is the melting-point of A and T' is any other temperature, then equation (2) becomes

$$d\ ln\left(\frac{x_L}{x_S}\right)_A = \frac{\Delta H_A}{R} \cdot \frac{-\ d\theta}{(T_A - \theta)^2} \qquad . \qquad . \qquad . \qquad (3)$$

Since ΔH_A varies with the temperature, equation (3) cannot be integrated except to express it in terms of ΔH_{A_0}, the heat of fusion of the pure solvent at its melting-point. However, we know from Kirchhoff's law that

$$\Delta H_A = \Delta H_{A_0} \pm \Delta C_P . \theta \qquad . \qquad . \qquad . \qquad (4)$$

where ΔC_P is the difference in the mean heat capacities of the solvent in the liquid and solid states. Strictly speaking, of course, ΔC_P is really the difference in the heat capacities of the reactants involved, but when the mol. fraction of the solvent is large compared to that of the solute, the heat capacities of the pure solvent in the liquid and solid states may be considered as identical wtth the heat capacities of the liquid and solid solutions. Combining equations (3) and (4) gives

$$d\ ln\left(\frac{x_L}{x_S}\right)_A = \frac{\Delta H_{A_0} \pm \Delta C_P . \theta}{R} \cdot \frac{-\ d\theta}{(T_A - \theta)^2} \qquad . \qquad . \qquad (5)$$

which upon integration between the limits $x_L = x_S = 1$ at T_A, when $\theta = 0$ and $x_L = x'_L$ and $x_S = x_S'$ when $\theta = T_A - T'$, gives

$$\int_1^{x_L', x_S'} d\ ln\left(\frac{x_L}{x_S}\right)_A = \frac{\Delta H_{A_0}}{R}\int_0^\theta \frac{-\ d\theta}{(T_A - \theta)^2} \pm \frac{\Delta C_P}{R}\int_0^\theta \frac{-\ \theta\ d\theta}{(T_A - \theta)^2}$$

$$ln\left(\frac{x_L'}{x_S}\right)_A = \frac{\Delta H_{A_0}}{R}\left(\frac{1}{(T_A - \theta)} - \frac{1}{T_A}\right) \pm \frac{\Delta C_P}{R}\left[ln\frac{(T_A - \theta)}{T_A} + \frac{\theta}{(T_A - \theta)}\right]$$

$$= \frac{\Delta H_{A_0}}{R}\left(\frac{1}{T'} - \frac{1}{T_A}\right) \pm \frac{\Delta C_P}{R}\left[ln\left(\frac{T'}{T_A}\right) + \frac{\theta}{T'}\right] . \qquad . \qquad (6)$$

By means of equation (6), the true heat of fusion of the solvent A at its melting-point can he obtained.[3] This is especially useful when the value of ΔH_A is small, as will be shown later in this paper. When there is no solid solubility, then the left-hand side of equation (6) becomes simple $ln\ x_L'$.

When the temperature interval is not large so that we can set $T'T_A$ to T_A, then with the aid of Maclaurin's theorem, equation (1) reduces to the simple Raoult-van't Hoff equation,

$$- \Delta T = \frac{RT_A^2}{\Delta H_A}(x_L')_B \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

and equation (2) likewise reduces to the so-called Planck equation,

$$- \Delta T = \frac{RT_A^2}{\Delta H_A}(x_L' - x_S')_B . \qquad . \qquad . \qquad . \qquad (8)$$

in which $(x_L')_B$ and $(x_S')_B$ represent respectively the molar concentration of the solute B in the liquid and solid phases. Equation (8) has very

[3] The term ΔH_A may represent the heat of transition, in fact any change of state.

limited applicability, especially with metallic solutions, because the melting-points of metals are generally high, in which case the degree of error can be minimized by not setting $T''T_A$ equal to $T_A{}^2$. Honda and Ishigaki [4] have used equation (8) in their study of the heats of fusion of metals, using, however, only 1 to 3 mol. per cent. solute.

In developing the various equations given above, we have tacitly assumed that the system behaves as an ideal solution, that is, one which obeys Raoult's law.[5] For example, we assume that the heat of solution (differential and integral) is equal to the heat of fusion, since we assume that the solution possesses the same *thermodynamic environment* as the pure liquid solvent at its melting-point. This is tantamount to saying that we assume the activity of the components (A and B) in the solid and liquid solutions to be directly proportional to their molar concentrations. In order that a system may obey Raoult's law so as to give an ideal solution, not only must the heat of mixture be zero, but the components must also mix without change in volume.[6] Lastly, we assume that there is neither dissociation nor association of the components in the course of solution and solidification.

The Iron-Carbon System.

It should be very interesting to investigate thermodynamically the iron-carbon system, which is perhaps the most important system studied. In Fig. 1 is shown part of the iron-carbon diagram above 1100° C. The
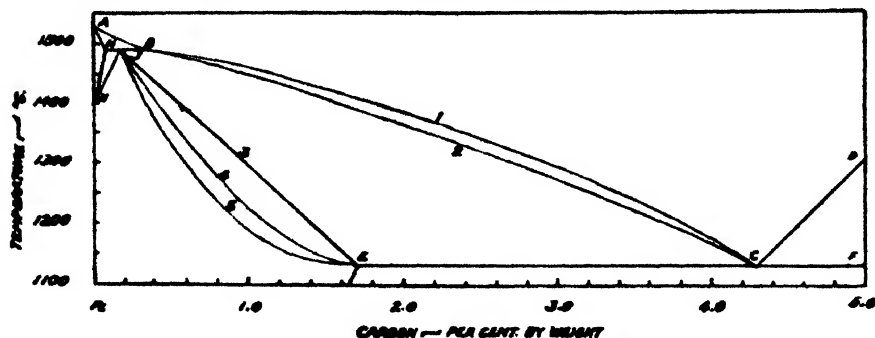
Fig. 1.—The iron-carbon constitutional diagram.

liquidus of the field obtained by Ruer and Klesper [7] is shown on a larger scale in Fig. 2. Note that it is slightly concave and that concentration of the triple point B is at 0·38 per cent. carbon, whereas Andrew and Binnie [8] determine it to be at 0·70 per cent. carbon. In the γ field, liquidus (1) is one obtained by Ruer and Goerens [9] (with slight temperature

[4] K. Honda and T. Ishigaki, *Sci. Repts., Tohoku Imperial Univ.*, 14, 219, 1925.

[5] For a comprehensive discussion of ideal solutions, consult Hildebrand : "Solubility," 1924. The Chemical Catalog Company, Inc., New York.

[6] According to the dictum of the Lewis school, if a system (A – B) forms a compound, it is no longer ideal. The present writer is unable to subscribe to this purely arbitrary dictum, because the phase rule definitely allows us to divide such a system into different parts, thus, A – A$_n$B and A$_n$B – B, when a compound A$_n$B is formed. Subtracting the heat of formation of A$_n$B (in the liquid state), the heat of mixture may actually be zero. Likewise, we can and should treat a system showing an allotropic transition as composed of two parts. For example, in the case of the iron-carbon system, we shall treat the field and the γ field separately.

[7] *Ferrum*, 11, 257, 1914.

[8] *J. Iron and Steel Inst.*, 119, 309, 1929.

[9] *Ferrum*, 14, 161, 1917.

correction to make it intersect the eutectic temperature of 1130° C. at 4·3 per cent. carbon). The other liquidus (2) is essentially after Honda and Endo [10] and Carpenter and Keeling,[11] corrected at higher temperatures to meet point B at 1487° C. (the peritectic temperature).

Carpenter and Keeling obtained essentially a straight solidus. When temperature corrections above 1416° C. are made in accordance with the suggestion advanced by Ellis,[12] it agrees with solidus 3 as shown in Fig. 1, which is also verified by the works of Andrew and Binnie,[8] Ellis,[13] and Jominy.[14] Solidus 4 is essentially that established by the Japanese school, while solidus 5 is the one obtained by Gutowsky.[15] The writer has already shown,[16] on the basis of magnetic analysis, that in the case of solidus 4, the Fe_3C in austenite has only partially dissociated, while in Gutowsky's case, the Fe_3C solute was not dissociated at all. The equilibrium (i.e., equilibrium with the melt) solidus is the straight solidus 3, from 0·18 to about 1·7 per cent. carbon at 1130° C.

Since in Fig. 1 we express the equilibrium relations in terms of weight per cent. carbon, it is, therefore, necessary to convert it to mol. per cent.

FIG. 2.—The " δ + Melt " field of the iron-carbon system.   (After Ruer and Klesper.)

composition. In Figs. 3 and 4 are shown the diagrams expressed in mol. per cent. carbon and mol. per cent. Fe_3C respectively. (The other solidus lines 4 and 5 have been omitted in order to avoid confusion.) We note that expressed in mol. per cent. carbon, the liquidus lines (Fig. 3) become quite convex, whilst in Fig. 4 the liquidus lines are concave, although liquidus 1 is very close to a straight line. Likewise note that the liquidus of the field becomes a straight line in Fig. 3, but it becomes appreciably concave when expressed in mol. per cent. Fe_3C (Fig. 4). On account of the steep slope of the solidus line, the deviation from linearity in Figs. 3 and 4 is slight.

[10] Sci. Repts., Tohoku Imperial Univ., 16, 627, 1927.
[11] J. Iron and Steel Inst., 65, 224, 1904.
[12] Metals and Alloys, 1, 462, 1930.
[13] Carnegie Schol. Mem., Iron and Steel Inst., 15, 195, 1926.
[14] Trans. Amer. Soc. Steel Treat., 16, 372, 1929.
[15] Metallurgie, 6, 731, 1909.
[16] Amer. Inst. Min. and Met. Engrs., Tech. Pub., No. 382, 1931.

It is implicit in equation *2* that when the liquidus is convex, the solidus should likewise be convex, *vice versa.* Since we have a straight solidus, then we should expect a straight liquidus line (or very nearly so). The implied relationship between the paths of the liquidus and the solidus lines

FIG. 3.—The iron-carbon constitutional diagram in mol. per cent. carbon. Derivative of Fig. 1.

is better illustrated in the unintegrated form, Planck's equation 8. By introducing the distribution constant of the solute between the liquid phase and the solid phase, that is, $\frac{k}{k'} = \left(\frac{dx_B}{dx_L'}\right)_B$, we obtain

$$dT = \frac{RT^2}{\Delta H_A}\left(1 - \frac{k}{k'}\right)(dx_L')_B \qquad . \qquad . \qquad . \quad (9)$$
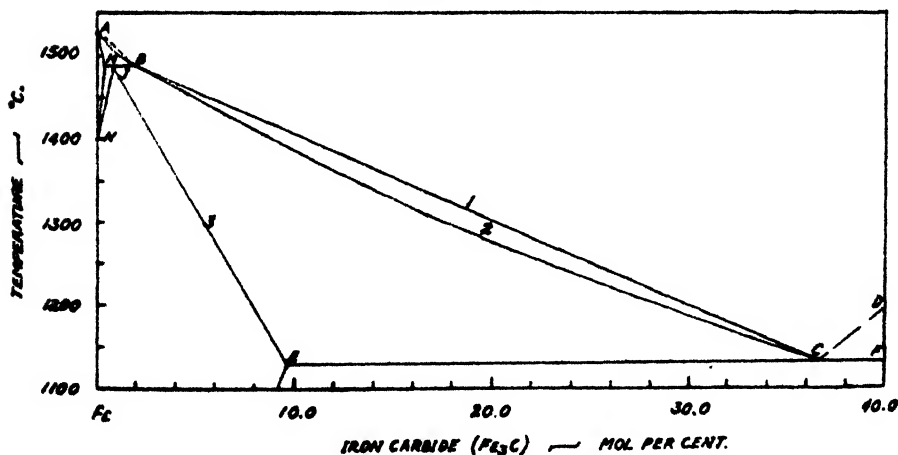
FIG. 4.—The iron-iron carbide constitutional diagram in mol. per cent. Fe$_3$C. Derivative of Fig. 1.

It is obvious from equation 9 that $(1 - k/k')$ cannot remain a constant, even for a very small temperature interval from the melting-point unless the shapes of the liquidus and the solidus are similar.[17] Moreover, if equations

[17] In the case of solid solutions, the term "ideal solubility curve" has become meaningless as each metal solute may have different distribution constants, k/k', depending perhaps on the internal pressures of the components involved.

2 and 9 hold at all, it should hold more strictly as the dilution increases. Hence, we conclude that the *solute in the melt must be* Fe_3C *and not carbon*, although we do not know the nature of the solute in the solid state without
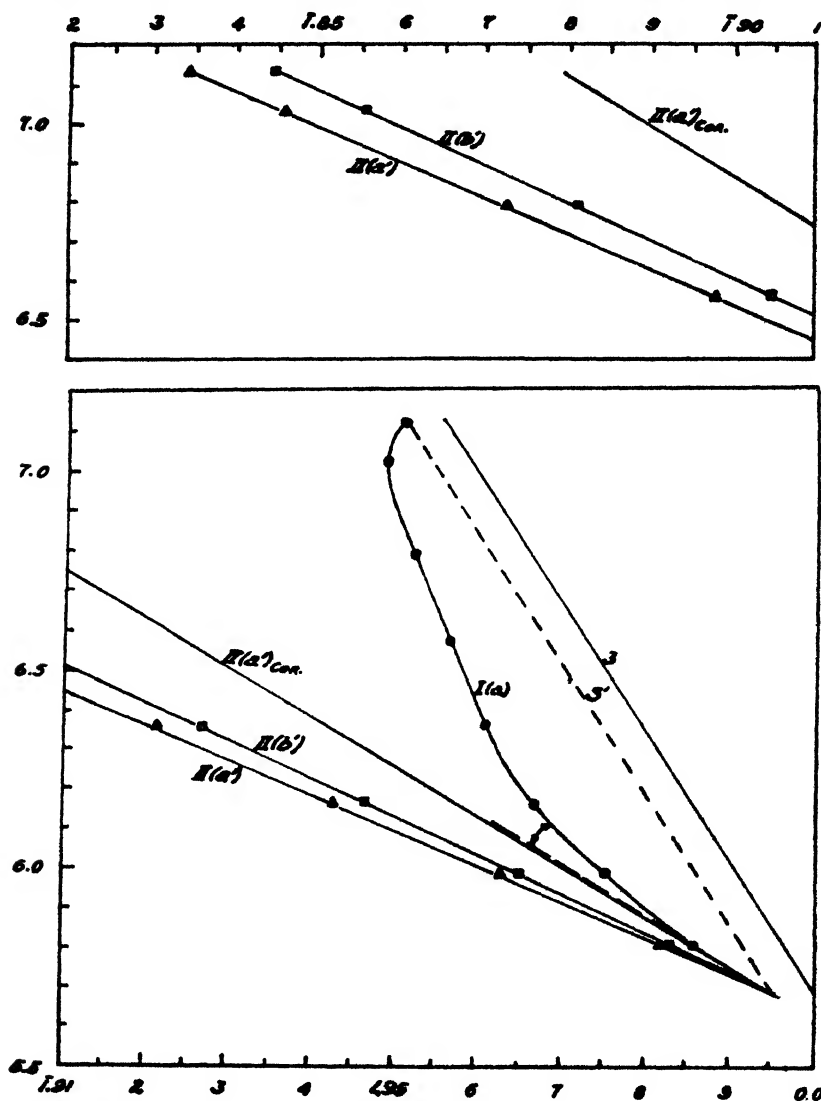
FIG. 5.—The $\log \left(\dfrac{x_L{'}}{x_S}\right)_{Fe}$ values in Tables I., II., and III., are plotted against $1/T$ according to equation 2. Curve 3′ (correction factor) is plotted according to equation 10, and then artificially move to coincide with curve 3, as we set Q (eq. 10) to zero at 1487° C. The slope of the II(a′)$_{cor}$. curve gives the true heat of fusion of γFe.

introducing evidence (as obtained by the writer) from other sources. If we had ever observed a pronounced convex solidus, then there would have remained the further possibility from Fig. 3 that the solute in the melt might be carbon.

On account of the fact that we are dealing with mol. per cent. concentrations of the solvent (iron), we are forced to make some arbitrary *a priori*

TABLE I.

(x_L)Fe, C.	(x_s)Fe, C.	$\log\left(\dfrac{x_L}{x_s}\right)$.	t.	$\dfrac{10^4}{T}$
Data on Curve I(a)				
82·72	92·57	I·95114	1130	7·12
83·05	92·93	·94918	1150	7·02
84·30	93·85	·95240	1200	6·78
85·82	94·80	·95668	1250	6·56
87·50	95·70	·96110	1300	6·35
89·55	96·65	·96687	1350	6·15
92·25	97·58	·97561	1400	5·98
95·35	98·50	·98588	1450	5·80
98·25	99·12	·99617	1487	5·68

TABLE II.

(x_L)Fe, Fe$_3$C.	(x_s)Fe, Fe$_3$C.	$\log\left(\dfrac{x_L}{x_s}\right)$.	t.	$\dfrac{10^4}{T}$.
Data on Curve II(b')				
63·20	90·37	I·84470	1130	7·12
65·20	90·86	·85588	1150	7·02
70·10	92·10	·88146	1200	6·78
75·00	93·33	·90504	1250	6·56
79·90	94·55	·92689	1300	6·35
84·70	95·80	·94651	1350	6·15
89·60	97·10	·96509	1400	5·98
94·50	98·30	·98288	1450	5·80
98·15	99·14	·99568	1487	5·68

TABLE III.

(x_L)Fe, Fe$_3$C.	(x_s)Fe, C.	$\log\left(\dfrac{x_L}{x_s}\right)$.	t.	$\dfrac{10^4}{T}$.
Data on Curve II(a')				
63·20	92·57	I·83425	1130	7·12
65·20	92·93	·84609	1150	7·02
70·10	93·85	·87329	1200	6·78
75·00	94·80	·89825	1250	6·56
79·90	95·70	·92164	1300	6·35
84·70	96·65	·94268	1350	6·15
89·60	97·58	·96295	1400	5·98
94·50	98·50	·98199	1450	5·80
98·15	99·18	·99547	1487	5·68

assumption regarding the processes occurring within the solution, especially in the assignment of the proper identity to the components taking part in the reaction. For example, we might begin by assuming with Cesaro[18] that

[19] *J. Iron and Steel Inst.*, **99**, 447, 1919.

iron is diatomic Fe_2 in the melt, although the very accurate work of Rode-bush and Michalek [19] on the heat capacity of iron at extremely low temperatures definitely excludes the possibility of iron being diatomic.[20] Or we might assume that in the melt we have $(Fe_3C)_n$ or even some other form iron carbide. As will be shown below from data on the specific volume of the iron-carbon melts, all these assumptions, being highly improbable, need not be considered here any further. Hence, we have only four methods of combination of the probable identity of the components in the iron-carbon alloys, viz. (1) that carbon exists as elementary carbon in the liquid state and (a) as carbon or (b) as Fe_3C in the solid state; and (2) that carbon exists as Fe_3C in the liquid state and (a') as carbon or (b') as Fe_3C. This is what the writer has done, as shown in Fig. 5 (Tables I.-III.).

Note that curve I(a) deviates considerably from linearity, although the first two points give a slope almost coincident with the expected theoretical slope. This agreement is purely fortuitous. It is noteworthy that part of the I(a) curve is linear, which suggests the deviation to be a constant function, indicating a definite change in the ratio of molar concentrations, or what is equivalent to it, a change in the total mol. fractions. This could be conceived to be brought about by the formation of a compound of either the solute or the solvent. The combination I(b) has not been included because, on the basis of the solute in the solid solution being Fe_3C, the resulting curve will be even worse both with respect to the deviation from linearity and to its slope. On the other hand, as is to be expected, curves II(a') and II(b') are linear, although their slopes give too high values of the heat of fusion of iron, II(b') being worse than II(a').

Although we have evidence from other sources not considered here against the assumption that the austenite just solidifying from the melt dissolves Fe_3C as the solute, nevertheless we shall discuss the possibility of II(b') being correct. As Mortimer [21] has shown, there are many cases in which the $ln(x_L') \cdot T^{-1}$ curve may be linear and yet be far from the ideal slope, giving the correct heat of fusion of the solvent. He has shown in a very interesting way that the ratio of the slopes of the observed curve to the ideal slope is also a function of the ratio of the relative internal pressures of the two components. The writer believes that it is difficult to apply Mortimer's explanation to the iron-carbon system, because we do not know how to evaluate properly the rôle of the internal pressure not only in the liquid state, but also in the solid solution. Moreover, the writer believes —and has quantitative figures—that the relative internal pressure of Fe_3C is probably about twice as high as that of iron, or at least higher than the ratio of 1·3.

The slope of curve II(a') gives 92 cal./g. as the heat of fusion of iron, although Oberhoffer and Grosse [22] and Umino [23] have determined it to be 64·38 and 65·65 cal./g. (These values are the heat of fusion of iron from the form, whereas the value calculated from the slope of curve II(a') is the heat of fusion of γFe.) The International Critical Tables : I., page 104 and II., page 458, give respectively 48 and 49·4 cal./g., which are, of course, incorrect.

[19] J. Amer. Chem. Soc., **47**, 2117, 1925.
[20] The writer has already shown elsewhere that the thermodynamic method outlined in this paper, is capable of determining the polyatomicity of certain metals (specifically, Sb_2 and Bi_2) in terms of energy change, where X-ray methods are indecisive. Cf. Amer. Inst. Min. and Met. Engrs., Tech. Pub., No. 397, 1931.
[21] J. Amer. Chem. Soc., **44**, 1416, 1922 ; **45**, 633, 1923.
[22] Stahl und Eisen, **47**, 576, 1927.
[23] Sci. Repts., Tohoku Imperial Univ., **18**, 91, 1929.

In the case of curve II(a') we have Fe_3C as the solute in the melt, but it dissociates to carbon upon solid dissolution ; hence, more heat is involved in the transfer of one mol. of iron from the melt than the partial molar heat of fusion of iron. The additional heat is, therefore, evidently from the dissociation of Fe_3C, which we know to be an endothermic compound. This additional heat, which we shall designate as Q can be calculated from the equation,

$$d \ln \left(\frac{x_L''}{x_S} \right)_{Fe} = \frac{Q}{R} d \left(\frac{1}{T} \right) \qquad . \qquad . \qquad (10)$$

in which x_L'' is the equivalent molar concentration of iron in the melt after the Fe_3C has dissociated to carbon. Its derivation can be shown as follows

On account of the solid solution the total mass-action constant $K = \frac{k_L}{k_S}$, in which k_L and k_S are the equilibrium constants of the reactions occurring in the melt and in the solid respectively. If we let p_L be the solution pressure when Fe_3C solute is dissociated to carbon in the melt and p_S the solid solution pressure, then the heat of reaction is simply

$$- Q = RT^2 \frac{d \ln \left(\frac{k_L}{k_S} \right)}{dT} = RT^2 \frac{d \ln \left(\frac{p_L}{p_S} \right)}{dT} \qquad . \qquad . \qquad (11)$$

From the law of partial pressure, we know that $p_L = p_C''/x_C'' = p_{Fe}''/x_{Fe}''$ and $p_S = p_C'/x_C' = p_{Fe}'/x_{Fe}'$ and as the system is in equilibrium, $p_{Fe}'' = p_{Fe}'$. Since we are only concerned with the heat of reaction involved in the solidification of one mol. of iron, we are consequently only interested in the change of the partial pressure of iron due to the dissociation of Fe_3C in the process of solid solution. Hence, in equation (11), we shall merely substitute p_{Fe}''/x_{Fe}'' and p_{Fe}'/x_{Fe}' in place of p_L and p_S, so that we obtain equation 10 as shown above, in which x_C'' (therefore, x_{Fe}'') is directly obtained from the carbon concentration along the straight liquidus B-C in Fig. 3, because under ideal conditions when Raoult's law is obeyed, the partial pressure of carbon in the melt, p_C'', is uniquely defined.

From evidence which will be presented below, the writer has concluded that in the field, the solute is carbon, but in γ field, the solute is, as has already been shown above, Fe_3C. Since the solidification of γFe (austenite) begins at the peritectic temperature (1487° C.), then the correction factor due to the additional heat Q should also begin at that temperature. Hence, in Fig. 5 the correction curve 3 is drawn such that it intersects the ordinate axis at 1487° C. Its real position is shown by the dotted curve 3'. The correct slope of II(a') can then be easily obtained by subtracting the slope of curve 3 (in terms of logarithm values, of course), giving finally curve II(a')$_{Cor.}$ as shown in Fig. 5. It will now be evident why curve 3' was moved to the right until it coincides with curve 3. We see [24] the correction factor due to Q is zero at 1487° C. From the slope of curve II(a')$_{Cor.}$ *we obtain 66·4 cal./g. as the heat of fusion of γFe, from which, subtracting the heat of transition of γ to Fe, we can obtain the heat of fusion of iron at its melting-point.*

We shall now calculate the heat of transition of γ to Fe. We shall use equation 6, which is expressed with different notations as follows :

$$2 \cdot 3 \log \left(\frac{x'}{x_\gamma} \right)_{Fe} = \frac{\Delta H_T}{R} \left(\frac{1}{T'} - \frac{1}{T_T} \right) + \frac{\Delta C_P}{R} \left[2 \cdot 3 \log \left(\frac{T'}{T_T} \right) + \frac{\theta}{T'} \right] \quad (6')$$

[24] As an engineer, the graphical method appeals to the writer. The explanation in words appears to him much less simple than the graphical picture shown in Fig. 6.

in which x' and x_γ' are the molar concentrations of iron in the and γ fields respectively, ΔH_T the molal heat of transition, T_T the temperature of transition and T some other temperature, which we shall take as 1487° C., the peritectic temperature. The carbon solubility in Fe at 1487° C. is only 0·07 and the corresponding solubility in the γFe is 0·18 per cent. (Ruer and Klesper). Hence $x' = 0·9968$ and $x_\gamma' = 0·9914$ in terms of molal concentration of iron. From the work of Umino[3] the difference in the heat capacities of and γFe is about − 0·0047 cal./g. or − 0·262 cal./mol. Substituting all the necessary values in equation 6', we obtain

$$2\cdot3\log\left(\frac{0\cdot9968}{0\cdot9914}\right) = \frac{\Delta H_T}{R}\left(\frac{1}{1760} - \frac{1}{1673}\right) + \frac{-0\cdot262}{R}\left[2\cdot3\log\left(\frac{1760}{1673}\right) + \frac{87}{1760}\right],$$

which solving for ΔH_T and dividing by 55·84, gives 2·17 cal./g. as the heat of transition of γ to Fe, which is slightly higher than Umino's value of 1·86 and Durrer's 1·94, but lower than Oberhoffer's and Grosse's datum of 2·531 cal./g. We may, therefore, safely conclude that the heat of transition is about 2·2 cal./g. so that accordingly the heat of fusion of pure iron directly from the δ form is 64·2 cal./g., which is slightly lower than Umino's datum of 65·65 but checks Oberhoffer's and Grosse's datum[25] of 64·38 cal./g.

We shall now calculate the heat of fusion and melting-point of iron from the data obtained by Ruer and Klesper of the "δ + Melt" field as shown in Fig. 2. The purity of their iron-carbon alloys appears to be unbelievably high—containing only 0·03 per cent. Cu and 0·001 per cent. S. Although in their set of experiments they claim the melting-point of pure iron to be 1528° C., actually by two methods of extrapolation, the melting-point has been determined to be only 1524° C. The melting-point of pure iron, according to Tritton and Hanson,[26] is about 1535° C. It has been known for some time that the Le Chatelier thermocouple is no longer reliable at very high temperatures, say above 1450° C.[27] For this reason, Andrew and Binnie[8] used a tungsten-molybdenum thermocouple and obtained a liquidus very much higher than the Ruer and Goerens liquidus. The former also obtained 1497° C. as the peritectic temperature as compared with 1487° C. obtained by the latter; from other sources of evidence, we have reason to believe that 1487 (+ 3)° C. is probably the correct one. From a study of Fig. 2 we note that actually the observed peritectic temperature is about 1482° C. If undercooling occurred, as indicated in Fig. 2, then the amount of undercooling should increase with the carbon concentration.

Since we do not know the precise path of the solidus curve in the delta field, the liquidus curve alone is shown (B) in Fig. 6. Assuming that the distribution law holds in this range of dilution and that the maximum solubility of carbon in δFe to be 0·07 per cent., curve A was drawn. Subtracting the slope of curve A from the slope of curve B, we obtain 40·9 cal./g. as the heat of fusion of iron, which is certainly too small. Note that the melting-point is located at 1524° C. When the Andrew and Binnie data was plotted likewise, the heat of fusion of iron was calculated to be about

[25] For a long time, the heat of fusion of iron has been accepted as 48-49 cal./g. (cf. International Critical Tables, I., 104 and II., 458). There are many empirical rules connecting the heat of fusion with the melting-point, but the simplest one, according to the writers's studies, is analogous to Trouton's Rule in regard to the entropy change upon vaporisation, namely, $\Delta H/T_F = 2\cdot0 - 2\cdot3$ cal./°K. This is, of course, derivative of Richard's rule: $\frac{1}{2} . 6\cdot4 \ T_F$. On the basis of either rule, the heat of fusion is found to be 64 to 69 cal./g.
[26] J. Iron and Steel Inst., 110, 90, 1924.
[27] In this connection consult the interesting paper by Ellis (op. cit.), footnote 11.

77·9 cal./g., which is too high. On the basis of the heat of fusion being 64·2 cal./g. as calculated previously and assuming that melting-point of ordinary iron (containing the same amount of impurities as are to be found in iron-carbon alloys) is 1528° C., the liquidus curve B′ was plotted as shown in Fig. 6. In this case, the concentration of the melt at the peritectic temperature is found to be 0·59 per cent. carbon, as previously stated by the writer.

That the observed solubility is less than the theoretical solubility will be claimed by the "internal pressure" school (Hildebrand and his pupils) as evidence of the correctness of their theory in regard to the rôle of internal pressures. Even setting aside the probable error in thermal analysis at high temperatures, there is still another strong argument against it. As pointed out to the writer by Belaiew,[28] his granulation hypothesis, which incidentally has received considerable experimental evidence, requires a

Fig. 6.—The molar concentrations of iron in δFe (A) and in the melt (B) plotted according to equation 2. Curves (A′) and (B′) are theoretically calculated on the basis of the heat of fusion being 64·2 cal./g.

value of B (Fig. 2) between 0·6 and 0·7 per cent. carbon. The writer's calculated value of 0·59 per cent. carbon agrees with the lower limit placed by Belaiew and hence, we are justified in concluding that undercooling in the Ruer and Klesper experiments must have been much more than indicated by their cooling curves. On the other hand, the tungsten-molybdenum thermo-couple used by Andrew and Binnie appears to give higher values than the actual temperatures involved.

Some Theoretical Discussions of the Results Obtained.

It would appear very strange to physical chemists dealing with aqueous solutions that the thermodynamic laws of ideal solutions are obeyed to such a large range of concentration and temperature. Our common experience with electrolytes in aqueous solutions leads us to the *a priori* conclusion that the laws of ideal solution will not hold even to a very small fraction of one mol. per cent. Honda and Ishigaki[4] have already successfully applied equation 8 (Planck's equation) to as high as 3 mol. per cent. in metallic solutions. According to the Debye-Huckel theory[29] electrostatic forces exist which are due to the ions that behave as charged particles, insulated

[28] *Private communication.*
[29] The writer is greatly indebted to Dr. T. Shedlovsky of the Rockefeller Institute (New York City, U.S.A.) for suggesting this interesting explanation.

from each other in the solvent of high dielectric constant (as water is), whereas in the case of metallic solutions we have an equipotential system, where these electrostatic forces are absent. So we would expect the deviation from ideality to be due entirely to different sources (e.g., difference in internal pressures, heat of mixture, change in the specific volume upon mixing, etc.) which would be only effective cumulatively at much higher concentrations and less effective at higher and higher temperatures. Hildebrand and his school emphasise the importance of the internal pressures, yet the writer found a number of systems showing a complete series of solid solutions, although the components have appreciably different internal pressures. The rôle of internal pressure appears to the writer to be less important with metals possessing high melting-points than with those of low melting-points.[30]

Any deviation from Raoult's law, as in the case of change in volume upon mixing two liquids, should become less and less as the temperature increases. From a study of the data obtained by Matuyama,[31] the writer found this to be actually the case, so that in the range of high temperature involved in iron-carbon melts, the effect will be very small. The volume change upon mixing can, as a matter of fact, be mathematically calculated from the heat of mixture, vice versa. From a study of the results obtained by Kawakami,[32] who has made an important study of the heat of mixture of molten metals, one may infer this may be a small factor. With low temperature metals, which have consequently small heats of fusion, the effect of the heat of mixture becomes an important factor in the calculation of the heat of fusion. Kawakami has shown that with the exception of Bi and Sb the heat of mixture has been found to be negative, that is, heat absorption, and the corresponding heat of fusion would become larger than the theoretical value. However, if anything, the Ruer and Goeren liquidus I (Fig. 4) shows a negative deviation, when on the basis of Raoult's law, we should expect a positive deviation.[33] The loci of the heats of mixture plotted against mol.-fractions are, according to Kawakami's study, convex curves, each having a maximum point at 0·5 mol.-fraction. Such a convex curve clearly implies that the *differential* heat of solution is not equal to the *integral* heat of solution. The linearity of curve $II(a')$ implies that the differential heat of solution is identical with the integral heat of solution. From these considerations, the writer feels justified in concluding that the heat of mixture in the iron-carbon system is unimportant.

There is an anomaly in the iron-carbon system which the writer is at present unable to explain. We note from the calculations above that in the field, the solute in the melt is carbon, but in the γ field, the solute is Fe_2C. The writer is well aware that many persons will take violent exception to such a view, yet confirmatory evidence has been presented by

[30] The results of this particular study will be published in the near future.

[31] Sci. Repts. Tohoku Imperial Univ., 18, 19, 1929.

[32] Sci. Repts., Tohoku Imperial Univ., 16, 915, 1927; 19, 521, 1930. Anyone interested in the application of the thermodynamic method to low-temperature metallic systems should consult the papers. He gives a formula for the heat of mixture in the solid state, which appears to be incorrect as it will not reduce to the Duhem-Margules equation. The difficulty of properly evaluating the influence of the heat of mixture lies in the fact that the heat of mixture in the molten state may not be equal to the heat of mixture in the solid state, taking into account, of course, the sum of the partial molal heats of fusion of both components. This is a subject being studied by the writer at the present time.

[33] Cf. Sackur: "A Textbook of Thermodynamics and Thermo-chemistry," p. 234. Trans. by G. E. Gibson, 1917. Macmillan & Co., Ltd., London.

Benedicks, Ericsson and Ericson,[34] who have studied the specific volume of iron-carbon melts, as shown in Fig. 7. We note that the specific volume of the melt increases rapidly at first (A-B) and then from B, the increase is much smaller, but linear with respect to per cent. carbon. On account of the small density of graphite A-B is consistent with the assumption that in this range, the solute must be carbon. On the other hand, when B-C is extrapolated to the composition of Fe_3C (6·67 per cent. carbon), the specific volume obtained is consistent with the expected value; hence, from

concentration B upwards, the solute in the melt must be Fe_3C. The linear character of B-C indicates that within this range of composition, *Fe_3C is practically undissociated* — a conclusion which we would have arrived long ago from free energy considerations.[35] It may be mentioned here that Benedicks *et al* found that the locus of the
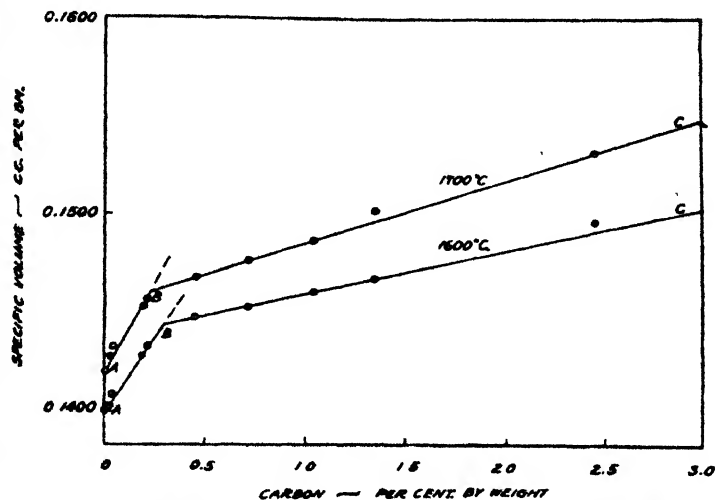
Fig. 7.—The change in the specific volume of molten iron-carbon alloys with increasing percentage of carbon by weight. (After Benedicks, Ericsson, and Ericson.)

specific volumes of iron-carbon alloys at their melting-points assumes almost identical shape as the Ruer and Klesper and Ruer and Goerens liquidus curves from the melting-point of iron to the eutectic composition. Note in Fig. 7 that B shifts to the right as the temperature decreases; at the peritectic temperature, 1487° C., B is located at 0·38 per cent. carbon in agreement with the results of Ruer and Klesper. It appears to the writer that the key to the study of the peritectic reaction in the iron-carbon system lies in the study of the anomalous behaviour of carbon in molten iron.

Other applications of the thermodynamic method will be shown in forthcoming papers.

Summary.

The thermodynamic laws of the depression of freezing-point of binary systems showing solid solubility, have been developed and discussed. It has

[34] *Jernk. Ann.*, 113, 423, 1929.
[35] The writer could never quite understand why the controversy regarding the "stability" of Fe_3C in the melt has been allowed to drag so long. If carbon has no affinity for iron, to use a slightly incorrect but better-understood term, then at what stage do they combine to Fe_3C, since we know the compound to be unstable at room temperature? Perhaps the misunderstanding lies in the meaning of the term, unstable. From thermodynamics, a compound is said to be stable when in the process of its formation there is a decrease in the free energy of the system.

been shown that the applications of the thermodynamic method to the iron-carbon system yields valuable information regarding the internal equilibria in both the liquid and solid phases. It is surprising to discover how closely the system obeys the thermodynamic laws of an ideal solution.

The heat of fusion of γFe has been calculated to be about 66·4 cal./g. and the heat of transition of iron : $\gamma \rightleftharpoons \delta$ has likewise been calculated to be 2·2 cal./g. ; hence, the true heat of fusion of Fe is 64·2 cal./g., which is in good agreement with the more reliable recent experimental values.

The liquidus of the "δ + Melt" obtained by Ruer and Klesper was also studied, but the calculated heat of fusion was determined to be only 40·9 cal./g. On the other hand the heat of fusion calculated from the data of Andrew and Binnie is too high, being 77·9 cal./g. Two sources of error in high temperature studies are : incorrect temperature readings and undercooling.

Some general but theoretical discussion on the interpretation of the results obtainable by thermodynamic methods of study, have been included in the hope that it might be helpful to others interested in similar studies of metallic systems.

The writer wishes to thank Professor Cecil V. King of Washington Square College, New York University, for much stimulating discussion on the various phases of the concept of an ideal solution, which has been very helpful in clarifying several points in this paper.

A THERMODYNAMIC STUDY OF THE IRON-CARBON SYSTEM IN THE SOLID AND LIQUID STATES.—II.

BY YAP, CHU-PHAY.*

The $\alpha \rightleftharpoons \gamma$ Transition.

In a paper to be presented elsewhere,[1] the writer has shown how on the basis of Sato's dilatometric data, *equilibrium* critical points (A_3 and A_{cm}) of iron-carbon alloys of comparatively high purity, can be derived, which appear to be of very high accuracy. By equilibrium critical point is meant that the transition temperature is theoretically determined at infinitely slow rate of heating and cooling. The A_3 critical points thus obtained by the writer are shown in Fig. 1 and the A_3 as well as the A_{cm} points are tabulated in Table I.

Note in Fig. 1 (*a*) that the A_3 point of pure iron is located at 900° C. and not at 910° C. as commonly believed; (*b*) that the eutectoid temperature, A_1, is at 720° C. and the eutectoid composition is at 0·795 or simply 0·80 per cent. carbon, although it is generally accepted to be around 0·90 per cent. carbon ; and (*c*) the A_{cm} line (not shown in Fig. 1) has been found to be very nearly a straight line on the basis of weight per cent. carbon. If we accept 1130° C. as the eutectic temperature, then the maximum solubility at that temperature is 1·685 per cent. carbon.

We shall proceed to study the nature of the $\alpha \rightleftharpoons \gamma$ transition and calculate the heat of transition. Note in Fig. 1 that the writer has drawn

the A_2 line through the iron-carbon range, including the austenite, after Honda's suggestion. Since Honda defines the A_2 point as the temperature at which iron finally becomes paramagnetic upon heating and *vice versa*, the concept of A_2 occurring before the A_3 and A_1 change taking place upon cooling is not inconsistent, provided we keep in mind the fact that *thermally* the main heat evolution corresponding to the A_2 (the heat of magnetisation) actually occurs after the A_3 and A_1 change. According to Fig. 1, the writer has drawn the A_2' line at 770° C., although A_2 is at 790° C. The lowering in the A_2 point may be conceived as due to the presence of Fe_3C in ferrite, similar to the case of the iron-silicon system. Yet at 770° C., the ferrite
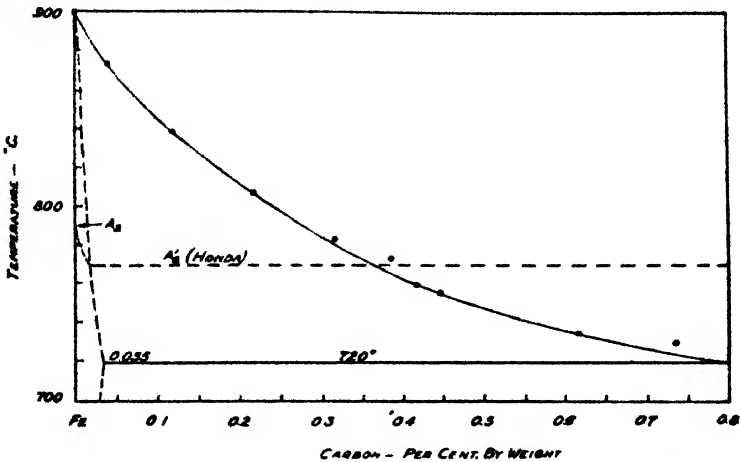
FIG. 1.—Critical points (A_3) of iron-carbon alloys in the austenite-ferrite range. (Values derived by the writer from Sato's data.)

only dissolves 0·02 per cent. carbon by weight, although its maximum saturation point is at 0·035 per cent. carbon. A similar case is found in the iron-zinc system.[2] It is possible that the solubility at 770° C. is already 0·035 per cent. carbon and from that temperature to 720° C. (A_1) there is no change in solubility in ferrite. It is also possible that above 0·02 per cent. carbon, the presence of Fe_3C in ferrite no longer affects the A_2 point. This point needs to be cleared up.

In Fig. 1 the ferrite solid solubility line has been drawn as a dotted line, not because it is not a phase-boundary line, but because we know nothing

TABLE I.—THE VALUES OF A_3 AND A_{cm} OBTAINED BY THE WRITER ON THE BASIS OF SATO'S EXPERIMENTS.

Steel No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Per Cent. C	0·00	0·04	0·12	0·22	0·32	0·39	0·42	0·45	0·62	0·74
A_3	900	873	838	807	783	773*	759	755	735	730*

Steel No.	11.	12.	13.	14.	15.	16.
Per Cent. C	0·92	1·07	1·12	1·24	1·33	1·55
A_{cm}	780*	856	870	925	968	1070*

² *Tech. Repts., Tohoku Imperial Univ.*, 8, 27, 1929.
* With an accuracy of ± (2 to 3)° C.

regarding its precise path. If we assume the distribution law to hold in this dilute range and accept 0·035 per cent. carbon as the maximum solubility of Fe_3C in ferrite, then if we simply plot the $\log(x_\gamma)$. T^{-1} of the

A_3 points, we can easily calculate the heat, transition. This is what has been done in Fig. 2 (Table I.) of and as expected the curve deviates considerably from linearity. From the slope of the first two points (with 0·04 and 0·12 per cent. carbon), the heat of transition is calculated to be 4·1 and 4·8 cal./g. of iron, which are too small compared to the best experimental values (given below).

On account of the very small heat of transition, the two sources of error which may give incorrect value of the A_3 heat of reaction are (a) inaccurate determination of A_3 points and (b) incorrect calculation of the true molar concentrations of iron in the iron-carbon alloys, containing a small but appreciable amount of impurities. The positive error (i.e., higher temperature) in (a) may completely counteract the error due to (b). Since, as stated above, the present writer believes most of the critical points tabulated in

FIG. 2.—The molar concentration of iron in ferrite (A) and in austenite (B), plotted according to equation 1. The final slope obtained by subtracting the slope of A from B should give the molal heat of transition of iron $\alpha \rightleftharpoons \gamma$.

Table I. are accurate to $\pm$ 1° C., the error due to (b) therefore becomes important, especially in the range of small carbon concentrations. The average impurities in the iron-carbon alloys used by Sato are :

0·055 % Si ; 0·02 % Mn ; 0·008 % P ; 0·04 % S≡0·123 % impurities.

Assuming that Mn forms MnS and the excess sulphur is in the form of FeS, P in the form of Fe_3P, the mol.-equivalents of the impurities on the basis of a 100 g. sample are :

0·1 % MnS ; 0·042 % FeS ; 0·026 % Fe_3P ; 0·197 % Si ≡ 0·00365 mol./100 g.

The amount of Fe bound up in the FeS and Fe_3P is equal to 0·0012 mol./100 g. Taking, as an illustration, Steel No. 4 (Table I.) which contains 0·22 per cent. carbon by weight, the amount of free iron, exclusive of the iron in the Fe_3C, is 100 − (0·22 − 0·123) = 99·657 per cent. by weight or 1·7843 mols./100 g. sample. Since 0·22 per cent. by weight carbon is equal to 0·01833 mol. of Fe_3C, the amount of iron bound up with the compound is 3 × 0·01833 = 0·055 mol. of Fe/100 g. sample. Adding the amount of iron bound up with the FeS and Fe_3P (that is, 0·0012 mol.), we finally obtain 0·0562 mol. of iron to be subtracted from the total amount of iron, 1·7843, which gives 1·7281 mols. of free iron acting as solvent. The

TABLE II.—THE MOLAR CONCENTRATIONS (CORRECTED AND UNCORRECTED) OF IRON ALONG THE A₃ LINE SHOWN IN FIG. 1. THE CORRECTED MOLAR CONCENTRATIONS OF IRON CORRESPOND TO THE TRUE ACTIVITY OF IRON IN THE SOLID SOLUTION, AUSTENITE.

No.	t.	x.	log 100x.	$10^4/T$.	log 100x.*	x.*
1	900	100·00	2·00000	8·527	—	—
2	873	99·82	1·99922	8·727	1·99830	99·61
3	838	99·43	1·99752	8·999	1·99660	99·22
4	807	98·95	1·99542	9·260	1·99449	98·74
5	783	98·46	1·99326	9·470	1·99233	98·25
6	773	98·10	1·99167	9·560	1·99074	97·89
7	759	97·95	1·99100	9·690	1·99007	97·74
8	755	97·80	1·99034	9·727	1·98941	97·59
9	735	96·90	1·98632	9·922	1·98538	96·69
10	730	96·27	1·98349	9·988	1·98250	96·05
E**	720	95·94	1·98200	10·071	1·98100	95·72

total mol.-equivalent in the 100 g. sample is 1·7281 + 0·0220 = 1·7501 mols., where 0·0220 is the sum of the mol.-equivalent of Fe₃C (0·01833) and of the impurities (0·00365). Hence, the true molar concentration of iron, which is equivalent to its *activity*, is 1·7281 ÷ 1·7501 or 98·74 per cent., as compared with 98·95 per cent. in the fourth column in Table II. In the same way, the values shown in column 7 are obtained, and plotted in Fig. 2.

Although we know that the change in the heat capacity of the solvent (iron) with respect to temperature should be considered in the present case, especially below the A_2' temperature, the existing data on the specific heat of iron are not sufficiently accurate to justify attempting to use equation 6 given in the first paper. The correction due to the change in the specific heat should be small for the first four points shown in Fig. 2 ; hence, we are fairly justified in drawing curve B, which gives about 5·5 (± 0·2) cal./g. as the heat of transition of pure iron. This is in fair agreement with Umino's [3] 5·6, Oberhoffer's and Grosse's [4] 6·77, and Wust and co-workers' [5] 6·56 cal./g.

The Differential Heat of Solution of Fe₃C in Austenite.

The heat absorbed when a small quantity of solute is dissolved in a given solution already containing a certain amount of the solute, is called the *partial* or *differential* heat of solution. When a mol. of the solute is dissolved in enough solvent to form a given solution, the heat absorbed is called the *total* or *integral* heat of solution. When the heat of dilution is zero, they are identical. We are interested in the differential heat of solution of Fe₃C in austenite above the eutectoid temperature (A_1).

The concept of the heat of solution of a solid in another solid is perhaps novel and requires some explanation. We know that when two liquids form an ideal solution, they should mix without any heat effect. We should clearly distinguish, however, the difference between a solid and a crystalline substance. In the present case, in dissolving Fe₃C (crystalline) in another

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* Corrected to take into account presence of various impurities in the iron-carbon alloys.
** Eutectoid composition, 0·8 per cent. carbon.
[3] *Sci. Repts., Tohoku Imperial Univ.*, 18, 91, 1929.
[4] *Stahl und Eisen*, 47, 576, 1927.   [5] *Zeit. Instrumentenkunde*, 39, 294, 1919.

crystalline substance, γFe, resulting in the destruction of the crystalline structure of the former, then is not the process tantamount to melting Fe_3C? Under ideal conditions, therefore, the heat of solution of Fe_3C in austenite should be the same as its heat of solution in the melt, taking into consideration, of course, the change in the heat capacities involved.

From equation 1 we know that if we plot the molar concentration of Fe_3C against $1/T$, the slope of the curve should then give the heat of solution of the compound in austenite, that is,

$$\frac{d \ln x_B}{d(1/T)} = \frac{\Delta H_B}{R} \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

In case there should be some solid solubility of Fe in Fe_3C, as claimed by Schwartz and his co-workers,[6] then we have to introduce the distribution constants in equation 1, thus

$$\frac{d \ln (x/x')_B}{d(1/T)} = \frac{\Delta H_B}{R} \qquad . \qquad . \qquad . \qquad (2)$$

in which x has the same significance as in equation 1, but x' is the molar concentration of the Fe_3C solid solution (containing dissolved Fe) in equilibrium with austenite. When there is no solid solubility of Fe in Fe_3C, then $x' = 1$, so that we revert to equation 1 above. Bates and co-workers[7] have made an attempt to determine the solubility of Fe in Fe_3C by means of planimetric measurements, but their meagre and contradictory results possess hardly any significance. From theoretical considerations, not to mention experimental evidence based on X-ray, density and chemical analysis, the writer cannot agree with Schwartz and his co-workers on the supposed solid solubility of Fe in Fe_3C.

At this point it is pertinent to insert an explanation as to why the writer has assumed the solute to be Fe_3C and not carbon as generally held. Without introducing any evidence from other sources, we will examine the implications of the A_{cm} line being straight (Table I.). A straight solubility line in this range of small concentrations of the solute, when the solubility can be expressed in any arbitrary units if desired, indicates that the heat of solution is constant from A_1 to the eutectic temperature, that is, $d\Delta H = 0$. From Kirchoff's equation, $d\Delta H/dT$ (in this case $d\Delta H/dT$ is not equal to the ΔC_P in equation 6), can only become zero if ΔC_P remains constant between any two temperatures. There is some evidence that Fe_3C at high temperatures, like many paramagnetic substances, has a linear or nearly constant specific heat both in the solid and liquid states; hence, $\Delta C_P \cong K$. On the other hand, if Fe_3C had dissociated upon dissolution in austenite, there would immediately occur a change in the value of C_γ. Hence, we are led to the conclusion that the solute in austenite must be Fe_3C and not carbon, as generally held.[8]

In Fig. 3 are shown the A_{cm} points tabulated in Table I. plotted according to equation 1. The reason a semi-log paper has been used is to show the relationship of the slopes of the log $x \cdot T^{-1}$ curve for the A_{cm} line to the slope of the log $x \cdot T^{-1}$ curve of the solubility of Fe_3C in the melt.

[6] *Trans. Amer. Soc. Steel Treat.*, **17**, 383, 1930.
[7] *Amer. Soc. Steel Treat.*, Preprint, 1930; not published in *Transactions*.
[8] The nature of the solute in austenite can also be inferred from specific heat studies, magnetic analysis, free energy calculations, etc. The writer also made an attempt (as shown elsewhere) of ascertaining the nature of the solute by the change in the partial pressure of CO_2 in contact with austenite of varying carbon concentrations.

The slope of curve 1 gives 5,720 cal./mol. as the heat of solution of Fe_3C in austenite.
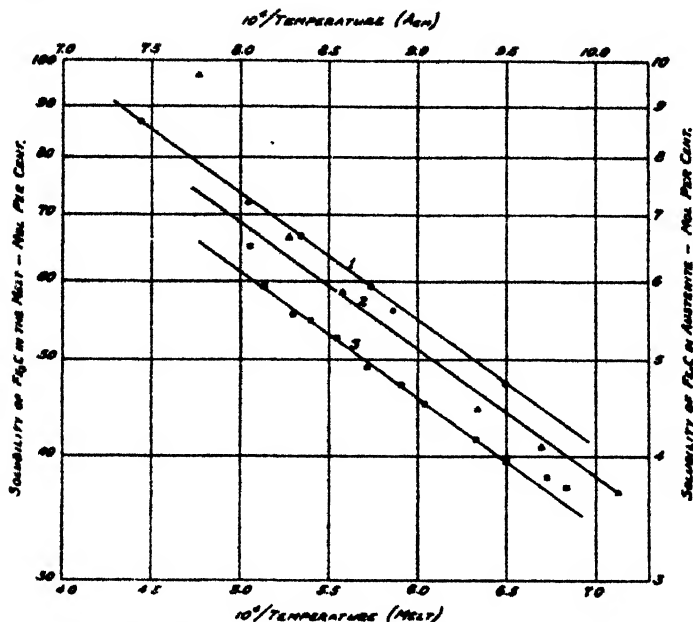
FIG. 3.—The solubility of Fe_3C in austenite (1) and in the melt (2 and 3). Note the parallel slopes of the solubility curves plotted according to equation 1.

The solubilty curve of Fe_3C in the melt has been determined by various investigators, as shown in Fig. 4. We shall not discuss here the reasons for Wittorf's [9] peculiar-looking solubility curve. Curve II. is based on the results of Hanemann,[10] and seems to be verified in the main at higher temperatures by Ruer and Biren.[11] Curve III. was obtained by Ruff and co-workers,[12] using perhaps the most elaborate experimental apparatus for their investigation. Hanemann and Ruer have the reputation for careful work, although their quenching method may give rise to an elevation in the actual temperature, which will result, of course, in the shifting of the Fe_3C solubility line to the left. Another important source of error, to which hardly any attention has been paid, is the effect of the furnace atmosphere on the equilibria in the melt.
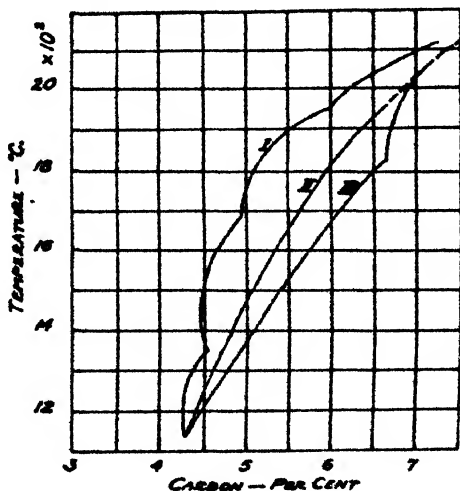
FIG. 4.—The solubility curve of Fe_3C in the melt at high temperatures, according to (I) Wittorf; (II) Hanemann, Ruer, and Biren; (III) Ruff and co-workers.

[9] Z. anorg. allgem. Chem., 79, 1, 1912.
[10] Ibid., 84, 1, 1914.   [11] Ibid., 113, 98, 1920.
[12] Ruff and Goeke, Metallurgie, 8, 417, 1911 ; Ruff and Borman, Z. anorg. allgem. Chem., 88, 397, 1914.

From free energy studies, the writer has concluded that the presence of oxygen in the melt together with the carbon oxides (gases) should displace the equilibrium in the direction of increased dissociation and consequently shifts the solubility line to the left also.

In Fig. 3 the results obtained by Ruff and co-workers (curve 2) are plotted together with the results obtained by Ruer and Biren (curve 3). The former was drawn through 4·3 per cent. carbon at 1130° C.; otherwise, it would have occupied a lower position. (The writer to be consistent has assumed 1130° C. and 4·3 per cent. carbon as the eutectic temperature and composition.) If there is any question regarding to the slope of curve 2, curve 3 should definitely dispel any doubt on that point. According to curve 2, the degree of dissociation of Fe_3C increases with the temperature. If Fe_3C possesses a true melting-point, then theoretically it is at around 2400° C.

From a study of Fig. 3, we are justified in concluding that the heat of solution of Fe_3C in the melt (fusion) is identical with its heat of solution in austenite. Although this is rather remarkable, it is not singular as the writer has also found this to be the case of Sb in the Pb-Sb system.[13] On the basis of this relationship, we should be able (a) to predict the ideal solubility curve of a solute, when the heat of solution and one point on the solubility curve are known, and (b) conversely to calculate the heat of fusion (approximate) from the equilibrium solubility curve experimentally determined. In a paper dealing with the surface energy of Fe_3C the writer[14] has developed an equation, based on a theory of supersaturation, which can be used to calculate the *equilibrium* solid solubility curve provided the heat of solution of the solute is known. As in many metallic systems, the solute might be an intermetallic compound, the relationship between the heat of solution and the heat of fusion enables us to calculate the heat of fusion from the solubility curve in the melt and set it equal to the heat of solution in the solid solution.

There is an apparent contradiction regarding the nature of the solute in austenite. In the first paper, the writer has shown that the solute in austenite in true equilibrium with the melt is carbon, but from the magnetic data of Honda and Endo, he found,[15] in agreement with the conclusion to be drawn from other sources, that the solute in austenite is Fe_3C. The writer further discovered that the difference in the nature of the solute lies in the fact that in the former, we have a case of cooling from the melt and in the latter, we are heating steels which have already reached room temperature (when Fe_3C is already formed) up to their melting-points again. The writer suggested that there probably occurs a transition in austenite at about 1020° C.—close enough to the thermal arrest observed by Carpenter and Keeling[16] at about 1050° C. Above 1020° C. the writer concluded the austenite is γ_C, but below that temperature, we have γ_{Fe_3C}. This change may be conceived to be a transition of a solid solution. The writer hopes in the near future to present further evidence on this point.

Finally, the difficulty of accepting the assumption of a transition in the austenite at 1020° C. lies in the fact that the A_{cm} line is almost perfectly linear. However, upon plotting in the proper scale in mol. per cent. Fe_3C, it is seen that although the first five (lower) points lie almost perfectly on a straight line, the last point (at 1070° C.) lies appreciably to the right

[13] *Amer. Inst. Min. Met. Engrs., Tech. Pub.* No. 397, 1931.
[14] To be presented before the Amer. Soc. Steel Treat. in September.
[15] *Amer. Inst. Min. Met. Engrs., Tech. Pub.*, No. 382, 1931.
[16] *J. Iron and Steel Inst.*, **65**, 224, 1904.

of the straight line. This may indicate a break in the A_{om} line, as required by the assumption of a transition in the austenite.[17]

Summary.

Application of the thermodynamic equation governing the depression of the transition point (melting or allotropy) to the $a \rightleftharpoons \gamma$ change in iron, indicates that the heat of transition is about 5·5 ($\pm$ 0·2) cal./g., which is in fair agreement with the more reliable experimental values varying from 5·3 to 6·77 cal./g.

The theory of the heat of solution of a solid in another solid, has been discussed and it was suggested that in an ideal system, the heat of solution of a solid solute in another solid solvent resulting, however, in the destruction of the crystalline form of the former, should be identical with the heat of solution of the solute in the melt (that is, heat of fusion).

Simple equations for the calculations of the heat of solution have been developed for cases when (a) the system shows solid solubility only at one end, and (b) the system shows solid solubility at both ends of the system. The heat of solution of Fe_3C in austenite has been calculated to be about 5720 cal./mol.

Two sets of solubility curves of Fe_3C in the melt have likewise been plotted and their slopes appear to be parallel to the curve of the Fe_3C solubility in the austenite. Hence, the heat of solution in the melt (fusion) is approximately equal to the heat of solution in the austenite, disregarding the small correction due to ΔC_P. The importance of this relationship (in a practical way) lies in the fact that knowing the heat of fusion of a compound or a metal, we should be able to predict the ideal solid solubility curve if we know but a single point and *vice versa*.

[17] It is perhaps needless to emphasise here that equilibrium diagrams expressed in per cent. by weight can be very misleading and that, as shown in the first paper, much can often be learned by simply converting them to mol. per cent. of the components. This, of course, involves the proper assignment of phases in equilibrium with one another in the melt and in the solid.

THE ELECTROSTATIC ENERGY OF DIPOLE MOLECULES IN DIFFERENT MEDIA.

BY RONALD P. BELL.

In the theory of electrolytes, considerable progress has been made by considering the ion as a charged conducting sphere surrounded by a continuous dielectric. In the absence of a net charge upon the molecule, the simplest static distribution of electricity is describable as a dipole, and the molecular model most susceptible to mathematical treatment is a rigid sphere with a doublet at its centre, the distance of separation of the doublet being infinitely small compared to the radius of the sphere. This model will be referred to as an ideal dipole molecule.

Martin[1] has employed as a model of a dipole molecule two oppositely charged spheres in contact. While such a model seems appropriate to the undissociated molecule of a mono-monovalent electrolyte, it is less suited to the general representation of a dipole molecule and does not lend itself to mathematical treatment. Thus in the calculation of the electrical energy of the system it is necessary to assume that each sphere is totally immersed in the medium, and to introduce an imaginary sphere around the

[1] Martin, *Phil Mag.*, **8**, 550, 1929.

doublet as a limit of integration. The spherical model employed here has the advantage of being capable of rigid treatment.

The change of electrostatic energy involved in transferring such a molecule from one medium to another has been previously discussed,[2] but the actual calculation offers certain points of difficulty. In the corresponding calculation for an ion [3] there is no field in the interior of the charged sphere, and integration from the surface of the sphere to infinity gives the total electrostatic energy. In the case of the ideal dipole molecule there exists inside the sphere a field which varies with the nature of the surrounding medium, and the energy of this field must be taken into account when considering the transfer of the molecule from one medium to another. This point is not taken into consideration in the author's previous paper.

Since the dipole is considered as being infinitely small, it is obviously impossible to attribute a value to the electrostatic energy of an ideal dipole molecule in any single medium. It should, however, be possible to calculate the difference between the energies in two different media, and if the model is feasible this difference should always be finite. It is clear that for this to be so, the dielectric constant in the neighbourhood of the dipole must not vary, and we shall consider that the dielectric constant inside the sphere (radius a) is always unity, while outside the sphere it has the value D of the medium in question.

Let V be the potential at a point r, θ referred to the centre of the sphere and the axis of the dipole. Then when the suffixes a and b refer respectively to the regions inside and outside the sphere, V_a and V_b must satisfy the following conditions :— [*]

(1) As $r \to 0$, $V_a \to \dfrac{\mu \cos \theta}{r^2}$.

(2) As $r \to \infty$, $V_b \to 0$.

(3) $\nabla^2 V_a$ and $\nabla^2 V_b$ are zero everywhere 'except at the centre and surface of the sphere.

(4) V and $D \dfrac{\partial V}{\partial r}$ are continuous across the surface of the sphere.

These conditions lead to the expressions

$$\left. \begin{aligned} V_a &= \frac{\mu \cos \theta}{r^2} \left(1 - \frac{2D - 2}{2D + 1} \cdot \frac{r^3}{a^3} \right) \\ V_b &= \frac{\mu \cos \theta}{r^2} \cdot \frac{3}{2D + 1} \end{aligned} \right\} \qquad . \qquad . \qquad . \quad (1)$$

Writing

$$\frac{2D - 2}{2D + 1} = \lambda,$$

the corresponding values of the field are

$$\left. \begin{aligned} E_a{}^2 &= \left(\frac{\partial V_a}{\partial r} \right)^2 + \frac{1}{r^2} \left(\frac{\partial V_a}{\partial \theta} \right)^2 \\ &= \mu^2 \left\{ \frac{1}{r^6} (1 + 3 \cos^2 \theta) + \frac{2\lambda}{r^3 a^3} (3 \cos^2 \theta - 1) + \frac{\lambda^2}{a^6} \right\} \\ E_b{}^2 &= \left(\frac{\partial V_b}{\partial r} \right)^2 + \frac{1}{r^2} \left(\frac{\partial V_b}{\partial \theta} \right)^2 = \frac{\mu^2 (1 - \lambda)^2}{r^6} (1 + 3 \cos^2 \theta) \end{aligned} \right\} \quad . \quad (2)$$

[2] Bell, *J. Chem. Soc.*, **139**, 1371, 1931.   [3] Born, *Z. physik.*, **1**, 45, 1920.
[*] The author is indebted to Mr. E. A. Guggenheim for this derivation of the potentials.

In calculating the change of electrostatic energy in transferring the molecule from a vacuum to a medium of dielectric constant D, we shall consider separately the changes inside (A_a) and outside (A_b) the sphere. Writing $E_a{}^1$, $E_b{}^1$ for the values of E_a, E_b in vacuo,

$$A_a = \int_0^\pi \int_0^a \frac{1}{8\pi}(E_a'^2 - E_a{}^2) \cdot 2\pi r^2 \sin\theta \, d\theta \, dr$$

$$= \frac{\mu^2}{4}\int_0^\pi \int_0^a \left\{ -\frac{2\lambda}{r^3 a^3}(3\cos^2\theta - 1) - \frac{\lambda^2}{a^6} \right\} r^2 \sin\theta \, d\theta \, dr.$$

The integral of the first term is zero, so that

$$A_a = -\frac{\mu^2 \lambda^2}{6a^3} \qquad \qquad \qquad (3)$$

which is finite for all values of D from 1 to ∞.

Similarly,

$$A_b = \int_0^\pi \int_a^\infty \frac{1}{8\pi}(E_b'^2 - DE_b{}^2) \cdot 2\pi r^2 \sin\theta \, d\theta \, dr$$

$$= \frac{\mu^2}{4}\int_0^\pi \int_a^\infty \frac{1}{r^4}\{1 - D(1 - \lambda)^2\}(1 + 3\cos^2\theta)\sin\theta \, d\theta \, dr$$

$$= \frac{\mu^2}{3a^3}\{1 - D(1 - \lambda)^2\} \qquad \qquad (4)$$

It will be noticed that while the energy of the external field decreases with increasing dielectric constant, that of the internal field increases. For the total change,

$$A = A_a + A_b = \frac{\mu^2}{6a^3}\{-\lambda^2 + 2 - 2D(1 - \lambda)^2\}$$

$$= \frac{\mu^2}{3a^3} \cdot \frac{D - 1}{2D + 1} \qquad \qquad (5)$$

and for the limiting case $D \to \infty$

$$A_{\text{max.}} = \frac{\mu^2}{6a^3} \qquad \qquad \qquad (6)$$

The corresponding expressions given by Martin [1] are

$$A = \frac{\mu^2}{3a^3}\left(1 - \frac{1}{D}\right) \qquad \qquad (7)$$

and

$$A_{\text{max.}} = \frac{\mu^2}{3a^3} \qquad \qquad \qquad (8)$$

For not too concentrated solutions we have

$$A = kT \ln_e S \qquad \qquad \qquad (9)$$

where S is the partition coefficient of the dipole substance between the liquid and the vapour phase. Since the picture we have employed is very idealised (particularly in respect of considering the solvent as a continuous fluid) we shall only expect to find any agreement with theory when the change of dipole energy is large compared with other effects. The magnitude of the discrepancies to be expected may be estimated by examining the data for the solubilities of the non-polar gases H_2, O_2, and N_2, which according to the present treatment would be assigned an equal solubility in all solvents. The maximum variations in the values of $\log_{10} S$ are in each case about ± 0.5. If we identify 'a' with the "kinetic radius" of the molecule, calculation from equations (6) and (9) shows that for the majority

of dipole molecules the maximum value of $\log_{10} S$ is less than unity, so that in general no agreement can be detected. The H_2O and NH_3 molecules, however, give values of approximately 4 and 2 respectively, so that in these cases we should expect a semi-quantitative agreement with theory.*

The experimental values of $\log_{10} S$ for water are plotted in Fig. 1.
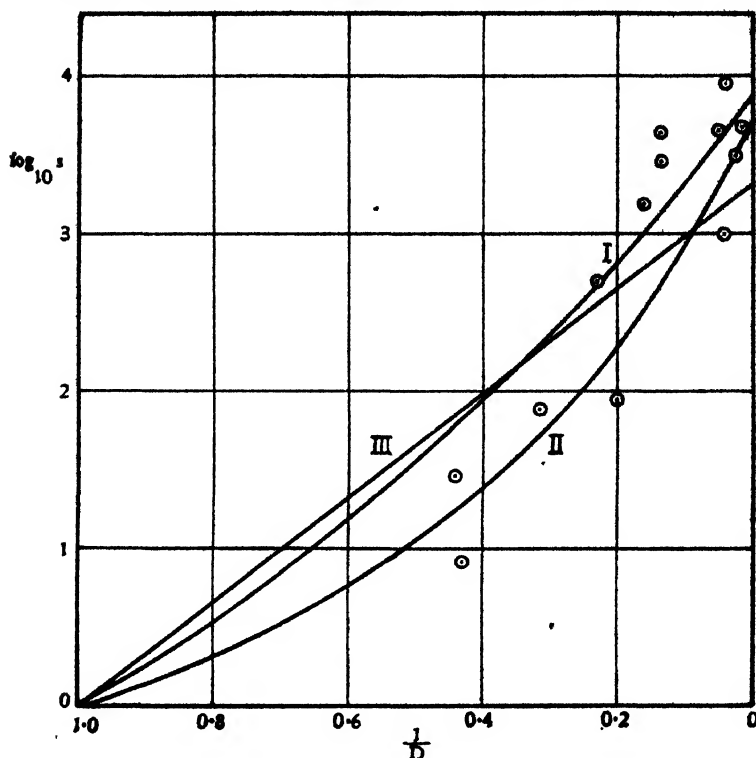
FIG. 1.

They are calculated from the solubilities at 20° given in International Critical Tables, with the exception of the value for ethyl alcohol, which is from the partial pressure of water in dilute solutions. Since none of the solubility values employed are greater than 10 per cent. by weight, the dielectric constant has been taken as that of the pure solvent. The figures are :—

Solvent.	$\text{Log}_{10} S$.	D.	$\frac{1}{D}$
Carbon tetrachloride	0·81	2·24	0·448
Benzene	1·46	2·28	0·440
Bromine	1·89	3·2	0·313
Ether	2·71	4·33	0·231
Chloroform	1·95	5·05	0·199
Ethyl acetate	3·20	6·4	0·156
Aniline	3·47	7·25	0·138
Methyl acetate	3·65	7·3	0·137
Methyl ethyl ketone	3·66	18·5	0·054
Epichlorhydrin	3·00	22·9	0·044
Ethyl alcohol	3·97	25·7	0·039
Furfural	3·51	41·9	0·024
Ethylene cyanide	3·69	66	0·015

* In the table previously given (Bell, *J.C.S.*, **139**, 1371, 1931) the values of $\log_{10} S_{\text{max.}}$ have been calculated without taking into account the internal field, and should be divided by two to give the correct values.

Curve I. (Fig. 1) represents equation (5) using the values $\mu = 1\cdot85 \times 10^{-18}$ and $a = 1\cdot17 \times 10^{-8}$. This value for a agrees well with the most recent values from viscosity determinations, $1\cdot14$ Å.[4] It will be seen that while the theory accounts well for the solubilities in liquids of high dielectric constant, the points for lower dielectric constants all fall below the line. Although the discrepancies are hardly greater than those anticipated, it is interesting to note that better agreement is obtained by a slight modification of the model employed.

If instead of taking the dielectric constant of the interior of the sphere as unity we assign to it a fixed value D_0, calculations similar to the above give :—

$$V_a = \frac{\mu \cos \theta}{D_0 r^2}\left(1 - \lambda_1 \frac{r^3}{a^3}\right),$$

$$V_b = \frac{\mu \cos \theta}{D_0 r^2}(1 - \lambda_1).$$

$$A = \frac{\mu^2}{6 D_0^2 a^3}\{D_0(\lambda_1'^2 - \lambda_1^2) + 2(1 - \lambda_1')^2 - 2D(1 - \lambda_1)^2 \quad . \quad (10)$$

$$A_{\text{max.}} = \frac{\mu^2}{2a^3(D_0 + 2)} \quad . \quad . \quad . \quad . \quad (11)$$

where

$$\lambda_1 = \frac{2(D - D_0)}{2D + D_0}, \qquad \lambda_1' = \frac{2(1 - D_0)}{2 + D_0},$$

Curve II. in Fig. 1 represents equation (10) with the values $\mu = 1\cdot85 \times 10^{-18}$; $a = 1\cdot00 \times 10^{-8}$ and $D_0 = 3$. It is seen that the points are on the whole better represented than by Curve I. It is doubtful, however, whether it is worth while introducing an arbitrary constant D_0 which has no obvious significance. Moreover, the value of a necessary in this case is rather low.

The straight line III represents Martin's expression (equation 7) with $\mu = 1\cdot85 \times 10^{-18}$; $a = 1\cdot47$ Å. Not only is the value of a much too high, but the straight line does not fit the results as well as either of the curves I or II.

The results for ammonia are shown in Fig. 2. They represent the author's own solubility determinations,[2] with the addition of values for ethyl alcohol, methyl alcohol and ether taken from International Critical Tables. The curves are :—

I. Equation (5) . $\mu = 1\cdot44 \times 10^{-18}$, $a = 1\cdot24$ Å.
II. Equation (10) . $\mu = 1\cdot44 \times 10^{-18}$, $a = 1\cdot00$ Å.
$D_0 = 3$.
III. Equation (7) . $\mu = 1\cdot44 \times 10^{-18}$, $a = 1\cdot48$ Å.

The best value of a from viscosity determinations is $1\cdot20$ Å.[4]

The state of affairs is thus similar to that found for water, except that the experimental points show the greater deviations anticipated. Again the spherical model gives better agreement and a more reasonable value for a than that of Martin, while the model with $D_0 = 3$ gives still better agreement, but rather too low a value for a.

It may be noted that equation (1) could be employed to calculate the force between two ideal dipole molecules in a solvent of given dielectric constant, and hence the deviations of such a solution from the gas laws. (The corresponding calculation for a dipole gas has already been carried

[4] Cf. Braune and Linke, Z. physik. Chem., A 148, 195, 1930.

out by Falkenhagen.)[5]   It has, however, been recently shown on the basis of quantum mechanics that in most cases intermolecular forces are chiefly due to an interaction between short period electronic vibrations, and that
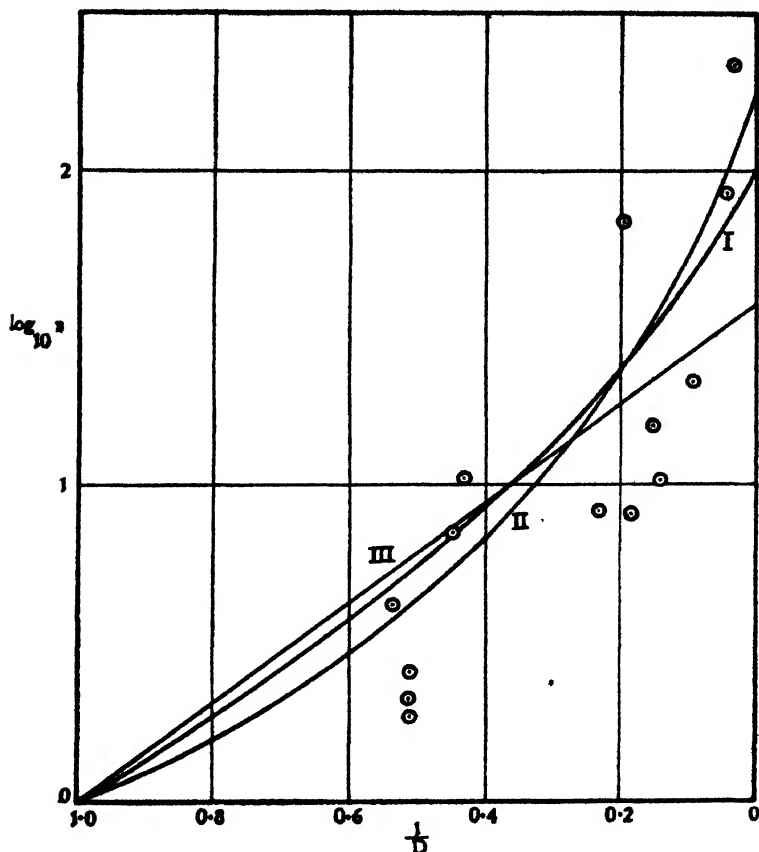
FIG. 2.

even for a molecule such as HCl, the presence of a permanent dipole plays a subordinate part.[6]   It is thus doubtful whether such calculations would have any value.

Summary.

(1) The change of electrostatic energy in transferring an ideal dipole molecule from one medium to another is calculated.

(2) It is shown that only in extreme cases is this energy change the determining factor for the distribution coefficients of dipole molecules.

(3) In the case of H_2O and NH_3 molecules there is a semi-quantitative agreement with the formula derived.

[5] Falkenhagen, *Physikal. Z.*, **23**, 87, 1922.
[6] London, *Z. physik.*, **63**, 245, 1930; *Z. physik. Chem.*, **B 11**, 222, 1930.

University Institute of Physical Chemistry,
Copenhagen.

CORROSION-FATIGUE TESTS OF MILD STEEL AND CHROMIUM-NICKEL AUSTENITIC STEEL IN RIVER TEES WATER.

By N. P. Inglis, Ph.D., M.Eng., and G. F. Lake, M.A.

It is now well known, chiefly through the work of Dr. McAdam, that a material subjected to even slight corrosion simultaneous with alternating stress may fail at stresses very much below the normal endurance limit. The definition of the ordinary fatigue or endurance limit for complete reversals of stress is the stress which can be reversed an indefinitely large number of times without failure. The "Corrosion-fatigue limit" in any corroding medium is defined as the stress which can be reversed an indefinitely large number of times without failure whilst the material is being acted upon by the corrosive medium. The corrosion-fatigue limit will, of course, depend upon the corroding medium operating. The present investigation of the subject was initiated owing to the cracking of certain mild steel shafts of pumps used to pump River Tees water at the works of Synthetic Ammonia & Nitrates, Ltd., at Billingham-on-Tees. The shafts in question had phosphor bronze impellers keyed on, and cracking took place where leakage occurred at the jointing between the sleeve and the impeller. Metallurgical examination of the cracked shafts showed that the material was quite up to specification and also that the material was not severely corroded. The examination revealed the presence of typical fatigue cracks, although the alternating stress in the shaft in service was certainly not more than ± 2 tons per square inch and was probably less. The failure was diagnosed as a corrosion-fatigue failure and experiments were put in hand to check this diagnosis and also to determine the resistance of corrosion-resistant steel (of the chromium-nickel austenitic class) to similar conditions.

Methods of Testing.

The fatigue testing machines used for the work were of the rotating beam type and are similar in design to those used by the Fatigue of Metals Laboratory at the University of Illinois.[1]

Fig. 1 is a photograph of the machine which is securely bolted on a steel slab which in turn is bolted on to a brick pillar in order to minimise vibration. The specimen is subjected to a uniform bending moment, and it is so designed that there is practically uniform stress over about $\frac{1}{4}$ inch in the centre of the span. With each revolution of the specimen the stress in any fibre of the metal undergoes one complete reversal from a value in tension to an equal value in compression and then back to the original value in tension. When it was desired to test the material under the combined influence of alternating stress and corrosion by River Tees water, the machine was run exactly as illustrated in Fig. 1, but a steady drip of a few drops per second of river water was allowed to fall on the centre of

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[1] See Univ. of Illinois Engineering Expt. Station Bulletin, No. 152.

the rotating test piece. The supplies of river water for these tests were always taken at high tide from the same spot. A typical analysis of the water is as follows :—

$$
\left.
\begin{array}{lll}
\text{Total solids} & . & 2954 \\
\text{Lime .} & . & 48 \\
\text{Magnesia} & . & 164 \\
SO_3 & . & 176 \\
Fe_2O_3 \text{ and } Al_2O_3 & . & 0\cdot4 \\
\text{Chlorine (as Cl)} & . & 1441\cdot0
\end{array}
\right\} \text{per 100,000 parts.}
$$

Tests Carried Out.

The following fatigue and corrosion-fatigue tests have been carried out :—

(1) Fatigue tests in air of mild steel and 18/8/1 Cr. Ni. W. steel (see specification below).

(2) Corrosion-fatigue tests of mild steel and 18/8/1 Cr. Ni. W. steel in River Tees water.

(3) Corrosion-fatigue tests in River Tees water of 18/8/1 Cr. Ni. W. steel which had been heated to 650° C. and cooled in air.

All the tests were carried out at room temperature.

Materials and Heat Treatment.

The mild steel used was good quality mild steel bar of about 0·20 per cent. carbon content and was normalised from 900° C. before machining the test pieces. The 18/8/1 steel was of the following specified com-position :—

$$
\begin{array}{lll}
\text{Chromium .} & . & 17 \text{ to } 19 \text{ per cent.} \\
\text{Nickel} & . & 8 \text{ to } 10 \text{ per cent.} \\
\text{Tungsten} & . & 0\cdot6 \text{ to } 1\cdot0 \text{ per cent.} \\
\text{Carbon} & . & \text{less than } 0\cdot16 \text{ per cent.}
\end{array}
$$

It was treated, in the form of $\frac{3}{4}$-inch bar, by heating to 1100° to 1150° C. and quenching in water in order fully to soften the material and thus put it into its most corrosion-resistant condition. The second set of experiments on 18/8/1 Cr. Ni. W. steel which had been heated at 650° C. was carried out on material which was fully softened initially and was then heated at 650° C. for one hour and air cooled from this temperature. It is now well known that when such a chromium-nickel austenitic steel as the above is heated in the range 500° to 900° C. and is not rapidly cooled, a constituent, probably carbide, is precipitated from the normal solid solution and the material is prone to disintegrate in an intercrystalline manner when subjected to many corroding-media. It is also known that the presence of the small percentage of tungsten minimises this defect, but it does not provide a complete cure, and heating for one hour at 650° C. will certainly cause this precipitation. It was thought wise to carry out tests on the material when in this improper condition of heat treatment primarily, because when large masses of this steel are cooled from the correct soften-ing temperature of 1150° C. the rate of cooling through the range 500° to 900° C. may not be sufficiently rapid to preserve the complete solution of carbides and the material is left in a condition which, according to the rate of cooling, is more or less prone to disintegrate. Numerous previous experiments had shown that the "maltreatment" given in the present case,

i.e. heating to 650° C. for one hour, would give the worst possible condition as regards disintegration.

Test Results.

The test results are given in Table I., and these results are plotted as "Stress-reversals Curves" in Figs. 2 and 3. The number of reversals is

TABLE I.—FATIGUE TESTS ON MILD STEEL.

Material.	Conditions of Test.	Semi-range of Stress. Tons/ins.²	Reversals to Fracture.	Remarks.
Mild Steel.	In air.	20·9	681,550	Broken
		19·4	4,388,200	Broken
		18·1	16,278,950	Broken
		16·5	11,500,000	Unbroken
	Estimated fatigue limit ± 17 tons/ins.²			
	Subject to drip of Tees river water.	18·1	227,300	Broken
		16·2	440,850	Broken
		11·8	3,498,200	Broken
		9·15	10,621,700	Broken
		7·1	10,242,500	Broken
		6·1	15,412,900	Broken
		4·0	28,483,250	Broken
		2·6	66,363,250	Broken
Fully softened 18/8/1 steel.	In air.	20·9	13,800	Broken
		18·85	37,650	Broken
		18·6	73,100	Broken
		17·6	25,858,500	Unbroken
		16·2	20,615,000	Unbroken
	Estimated fatigue limit ± 17·6 tons/ins.²			
	Subject to drip of Tees river water.	17·7	287,550	Broken
		15·8	7,288,200	Broken
		15·8	1,694,650	Broken
		14·6	1,235,200	Broken
		13·5	4,303,400	Broken
		12·8	22,366,300	Broken
		12·0	3,804,000	Broken
		11·1	100,000,000	Unbroken
	Estimated corrosion-fatigue limit ± 11·2 tons/ins.²			
18/8/1 steel heated for one hour at 650° C.	Subject to drip of Tees river water.	17·7	1,368,050	Broken
		15·8	3,282,400	Broken
		12·9	9,043,950	Broken
		10·1	6,751,400	Broken
		8·35	25,593,000	Broken
		6·40	150,000,000	Unbroken

plotted logarithmically as the abscissæ as this is found to be the most convenient method of plotting fatigue test results.

From Fig. 2 the very big difference between the fatigue limit in air and the corrosion-fatigue limit in River Tees water is at once apparent. The fatigue limit in air is about ± 17 tons/ins.², whilst the corrosion-fatigue limit in Tees river water is practically nil, since failure took place after 66,000,000 reversals of 2·6 tons/ins.² and the S-N curve shows no indication of becoming asymptotic to a limiting stress. From this curve it will be

seen that mild steel subjected simultaneously to an alternating stress of only ± 1 ton/ins.^{2} and a drip of Tees river water will fail after about 120,000,000

FIG. 2.
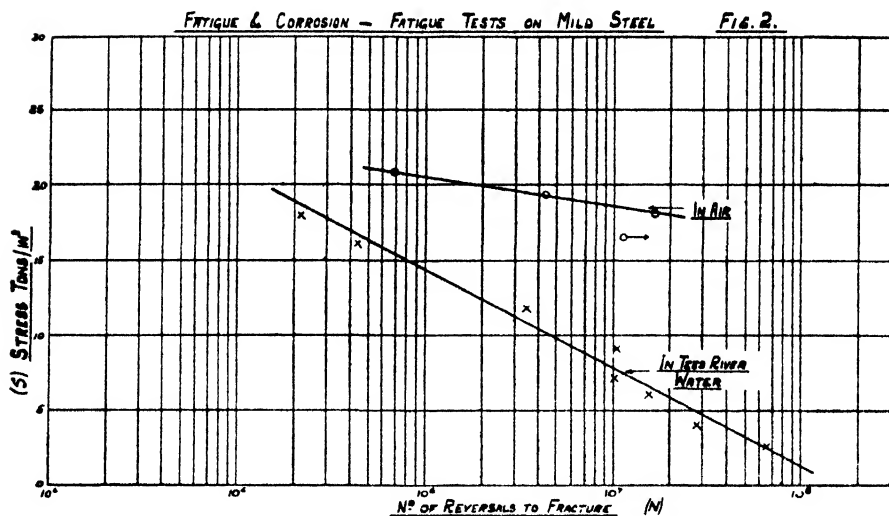
reversals.   (In the case of a pump shaft running at 475 r.p.m. this would correspond to a life of about 5 months.)

It would, therefore, seem that if mild steel is subjected to the simultaneous action of Tees river water and alternations of stress, no matter how small the stress may be, failure will ultimately occur.
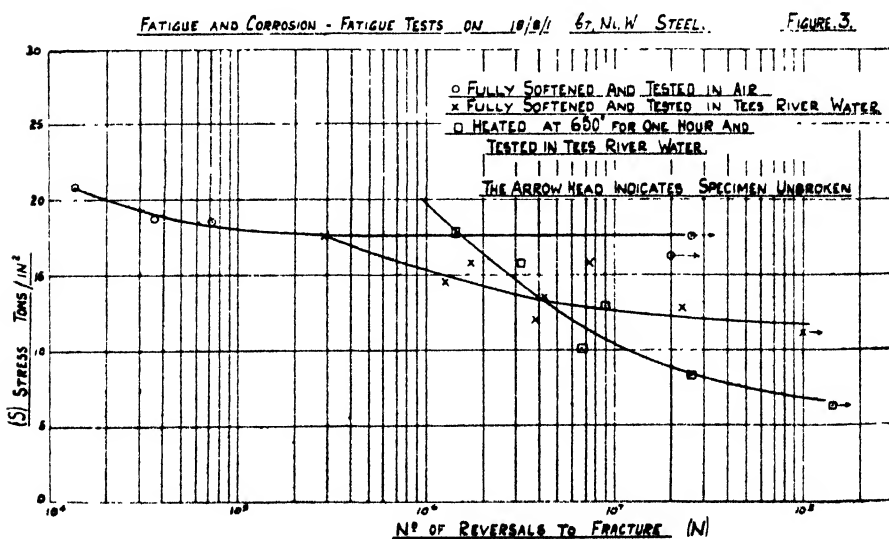
FIG. 3.

In the fully softened (*i.e.* the correctly heat treated) condition, 18/8/1 Cr. Ni. W. steel has a fatigue limit in air of ± 17·6 tons/ins.^{2} (see Fig. 3). The corrosion-fatigue limit of this steel in this condition in river Tees water is ± 11·1 tons./ins.^{2} so that, whilst there is a very appreci-

Fig. 1.

Fig. 6.—... Cr Ni W. steel previously air cooled from 650° C. Failed after 6,51,400 reversals of 10.1 tons in.² with water drip.

Fig. 5.—... Cr Ni W. steel previously air cooled from 650° C. Failed after 6,79,000 reversals of 15 tons in.² with water drip.
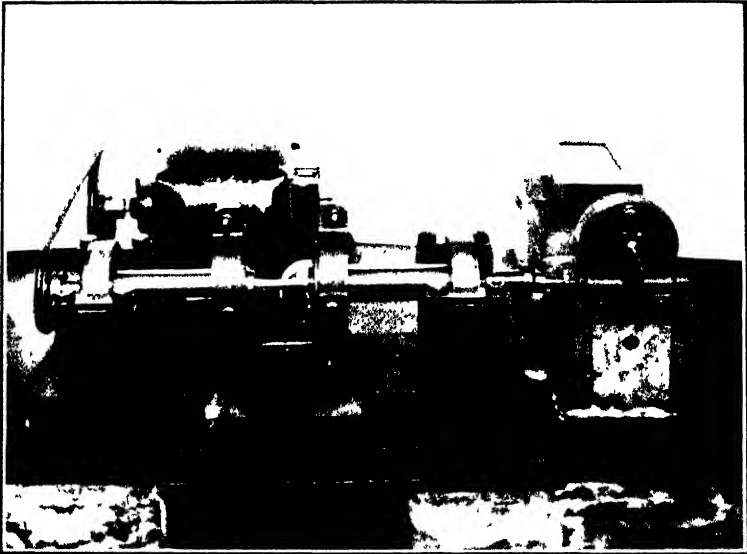
Fig. 4.—Mild steel. Failed after 440,850 reversals of 10.2 tons ins.⁻... th water drip. 4-5.

able reduction due to the water drip, the reduction is not nearly so great as in the case of mild steel. When the 18/8/1 Cr. Ni. W. steel was put into an incorrect condition, by heating to and cooling from 650° C., the corrosion-fatigue limit was reduced to approximately ± 6·5 tons/ins.² The actual fatigue and corrosion-fatigue limits obtained may, therefore, be summarised as follows :—

Material.	Fatigue Limit in Air. tons/in.2.	Corrosion-fatigue Limit in Tees River Water. tons/in.2.
Mild steel	± 17·0	Nil
18/8/1 Cr. Ni. W. steel (fully softened)	± 17·6	± 11·1
18/8/1 Cr. Ni. W. steel heated to, and cooled from, 650° C. . .	[± 17·6] *	± 6·5

It must be clearly realised that failure by corrosion-fatigue is not merely a matter of reducing the section of the stressed material nor is it entirely due to the increase in applied stress caused by the formation of corrosion pits. The reduction in diameter is quite negligible, the specimens being covered with a light surface rust only. The 18/8/1 Cr. Ni. W. steel specimens which had failed in the water drip fatigue test were quite unattacked and there was no visible pitting or even surface staining. After tests to destruction the 18/8/1 Cr. Ni. W. steel specimens subjected to the water drip seemed to be in exactly the same condition as those tested to destruction in air.

Microscopic Examination.

Several of the broken specimens were cut longitudinally, set in Wood's metal in order to protect the fractured edge during polishing, and carefully polished. They were then examined microscopically and Figs. 4 to 6 are microphotographs showing the fractures. It was found that in all cases the fractures are predominantly transcrystalline and the microphotographs shown are quite typical of a large number examined.

It is well known, of course, that ordinary (air) fatigue failures are transcrystalline, but there is less information regarding the type of fracture caused by corrosion-fatigue. The fact that these corrosion-fatigue failures are predominantly transcrystalline is of particular interest, since purely corrosion cracks are usually intercrystalline. This indicates that fatigue is the final cause of failure, although the initiation of the first cracks may be intercrystalline fissuring caused by corrosion. If intercrystalline fissuring is the cause of the initial formation of a crack, which is subsequently propagated by fatigue, the intercrystalline portion of the crack is extremely small, since in all the specimens examined the fracture is essentially transcrystalline throughout. The fact that the corrosion-fatigue fracture of the 18/8/1 Cr. Ni. W. steel, previously heated at 650° C., is also transcrystalline is especially interesting, since the effect on this steel of heating at 650° C. is to precipitate a constituent, from the normal solid solution, at the grain boundaries which results in intercrystalline cracking when the material is in

* The fatigue limit in air of the 18/8/1 steel treated in this manner has not been actually determined, but it is probably the same as that of the fully softened steel, since heating at 650° C. does not seem to affect the purely mechanical properties.

contact with most corroding media.   Consequently, since the corrosion-fatigue limit of the material so heated is quite definitely less than that of the material fully softened and the effect of such heating is to weaken the material in an intercrystalline manner, it would be expected that the corrosion-fatigue failure would be at least largely intercrystalline.   However, as Fig. 6 very clearly shows, this is not the case.   The reduction in corrosion-fatigue limit by the 650° C. treatment has probably therefore been caused by the more rapid initiation of an intercrystalline crack at the surface of this improperly treated material and this crack has then been propagated in the manner described below.

Suggested Mechanism of Corrosion-Fatigue.

The suggested probable mechanism of this type of failure (based on the views expressed by McAdam, Evans, and others) is as follows : The effect of the repetitions of stress is to cause a continual breaking of the surface passive film and this allows the corroding liquor to form "pits" in the metal.   These "pits" may not necessarily be corrosion pits in the usual sense of the word but may take the form of minute intercrystalline fissures.   As soon as these pits or fissures are formed the stress is very greatly increased due to the high intensification at the root of such a pit or fissure.   This increase in stress causes increased attack by the corroding liquor owing possibly to the even readier breakdown of the passive film. In this way the stress and the corroding media have mutually intensifying effects and when the stress is increased in this manner above the normal fatigue limit failure proceeds by ordinary fatigue.   This theory seems to fit the observed facts very satisfactorily since the theory indicates the high corrosion-fatigue limit of the 18/8/1 Cr. Ni. W. steel owing to the very much more robust passive film formed on this steel, which would not be so easily broken by the repetitions of stress as in the case of many other metals.   It also fits the discovered fact that the corrosion-fatigue limit of the 650° C. treated material is less than that of the fully softened material, since the grain boundary weakness imparted by the 650° C. treatment will naturally tend to more rapid development of fissures and consequently more rapid intensification of stress.   (This theory is generally in agreement with that advanced by McAdam, see *Proceedings American Institute of Mining and Metallurgical Engineers*, 1928, and *Proc. American Society for Testing Materials*, 1929.)

THE ELECTRODEPOSITION OF CHROMIUM FROM TERVALENT CHROMIUM SALT SOLUTIONS. PART I. CHROMIUM CHLORIDE AND CHROMIUM SULPHATE BATHS.

By HUBERT THOMAS STANLEY BRITTON AND OLIVER BRENTWOOD
WESTCOTT.

Metallic chromium is nowadays almost exclusively electrodeposited from chromic acid solutions. Müller and Ekwall,[1] however, were unable to deposit chromium from highly purified chromic acid solutions, but were able to do so as soon as some sulphate was introduced. Whether the sulphate is in some way essential in facilitating the reduction of sexavalent chromium at the cathode to tervalent ions from which deposition of the metal ultimately takes place, remains an unsolved problem.[2] Considerable reduction does occur, and it is a significant fact that many chromic acid baths have been patented which contain appreciable amounts of tervalent chromium.[3]

Although chromium was first deposited from solutions of chromium salts by Junot,[4] and Bunsen,[5] and subsequently by Geuther,[6] from chromic acid, it was some time after the publication of the work of Sargeant [7] and Carveth and Curry [8] in which it was demonstrated that really satisfactory chromium deposits could be secured from chromic acid solutions, that the use of sexavalent chromium baths found commercial application. Regarding the use of tervalent chromium salt solutions, many patents were taken out prior to 1900,[9] whilst since this research was begun two other patents have been published.[10]

The various processes that have been described for the electrodeposition of chromium from tervalent salt solutions will be briefly considered.

Bunsen obtained bright metal by electrolysing a solution of chromous and chromic chlorides in a diaphragm cell, using a high cathode current density at 100°. Placet and Bonnet claimed to be able to deposit chromium from various salt solutions without the use of a diaphragm. In one patent they advocated the inclusion of alkaline earth and alkali metals, apparently to increase the conductivity of the electrolyte. A similar process was adopted by Moeller and Street, who used a solution of chrome alum and sodium sulphate as catholyte and sulphuric acid as

[1] *Z. Elektrochem.*, **35**, 84, 1929.
[2] See, however, Stscherbakov and Essin, *ibid.*, 1929 ; Roudnick, *ibid.*, 249, 1929.
[3] Salzer, D.R.P., 221,472, 1910 ; Grube, U.S.P., 1,496,845 ; Liebreich, D.R.P., 398,054 ; Le Bris, Br. Fr., 590,777 ; Suzuki, U.S.P., 1,600,076.
[4] B.P. 1183/1853.   [5] *Pogg. Annalen*, **91**, 619, 1854.
[6] *Liebig Annalen*, **99**, 314, 1856.   [7] *J. Physical Chem.*, **9**, 236, 1905.
[8] *Trans. Amer. Electrochem. Soc.*, **37**, 479, 1920.
[9] Placet and Bonnet, B.P. 19,344/1890 22,854-5/1892 ; Moeller and Street, B.P. 18,743/1899 ; Marino, U.S.P., 607,646/1898.
[10] The Ternstedt Mfg. Co. (B.P. 292,094/1929) and Langbein-Pfanhauser Werke A-G (B.P. 301,478/1929).

anolyte. They used a *C.D.* of 40 amp./dm.^{2} at 70° C. Le Blanc [11] endeavoured to repeat the work of Placet and Bonnet, but probably owing to the vagueness of their directions was unable to obtain chromium deposits. Using a diaphragm cell, and *C.D.*'s of 20-30 amp./dm^2. at 30°-80°, he obtained slight metal deposits from chromium sulphate solutions to which substances, such as sodium bisulphate and ammonium fluoride and hydrochloric acid had been added. Cowper-Coles [12] also used an acidified bath in order to prevent the deposition of basic matter. He used a 25 per cent. chromium chloride solution to which had been added a drop of hydrochloric acid. By using a *C.D.* of 4·5-5·5 amp./dm^2. at 90° C., he was able to get satisfactory deposits.

Férée [13] experimented with similar solutions, with the difference that he used a diaphragm. Whilst a simple solution of chromium chloride proved useless, the inclusion of hydrochloric acid appeared to assist deposition. Better results, however, were obtained by using a solution 1M. with respect to chromium chloride and 3M. with respect to potassium chloride. A remarkably high current efficiency of 45 per cent. is reported. Neumann and Glaser [14] studied chloride, sulphate and acetate baths in a two-compartment cell, mineral acids or salt solutions being used as anolytes. They state that metal was deposited from chloride solutions containing 100 grams of chromium per litre at current efficiencies up to 40 per cent. Temperature had very little effect on the efficiency. Sulphate solutions gave very similar results, but those of the acetate gave poorer yields. Carveth and Mott [15] made a detailed investigation of the deposition from catholytes of chromium chloride and chromium sulphate, using solutions of one of the following : potassium chloride, potassium hydroxide, sulphuric acid, ferrous ammonium sulphate, sodium oxalate, ammonium hydroxide, as anolytes. Except when sulphuric acid was employed as the anolyte, they found that the current efficiency obtained when chromium chloride as catholyte was subjected to repeated electrolysis, gradually increased to a maximum value, and then fell. With the sulphuric acid anolyte the efficiency became smaller. The fact that the current efficiency tended to increase in the former instances was considered to be due to the gradual attainment of an equilibrium between chromic and chromous ions. The true explanation, in all probability, lies in the effects produced in the catholytes by the increase in the amounts of the anolytes that diffuse through the diaphragm. In 1910, Voisin [16] was unsuccessful in his attempt to repeat the work of Placet and Bonnet, though he secured a current efficiency of 45 per cent. from a chromic chloride bath containing potassium chloride, as recommended by Férée. Some experiments were made by Sigrist, Winkler, and Wantz.[17] They concluded that in order to obtain satisfactory metal deposited from either chromium sulphate or chromium chloride solutions, it was necessary to interpose a diaphragm between the electrodes. According to these workers, the quality of the metal thus deposited, however, is always inferior to that obtained from a chromic acid bath. The deposits were of doubtful purity. While the

[11] *The Production of Chromium and its Compounds by the Aid of the Electric Current.*

[12] *Chem. News*, 81, 16, 1900.   [13] *Bull. Soc. Chim.* (3), 25, 614, 1901.

[14] *Z. Elektrochem.*, 7, 656, 1901.   [15] *J. Physical Chem.*, 9, 236, 1905.

[16] *Rév. Metallurgie*, 7, 1137, 1910.

[17] *Arch. Soc. phys. nat. Geneva*, 1924 (S), 6, Suppl. 112 ; *Helv. Chim. Acta*, 7, 968, 1924.

present work was being done, there appeared a paper by Pamphilov and Fillipitchev,[18] who have investigated deposition at ordinary temperature from various basic chromium sulphate solutions. Generally speaking, their deposits were unsatisfactory, and current efficiencies low. As regards current efficiency, their data indicated that a large concentration of highly basic chromium sulphate is necessary. Unlike Carveth and Mott, they do not consider that chromous ions are necessary.

In regard to the two recent patents, that of the Ternstedt Mfg. Co., which specifies a chromium chloride bath to which large quantities of alkali chlorides have been added, is very similar to baths already investigated, for example, by Férée. That of the Langbein-Pfanhauser Werke A-G. emphasises the importance of regulating the hydrogen ion concentration of tervalent chromium salt baths to p_H 4-6 by means of salts of organic acids and boric acid.

Theoretical Considerations.

A study of the previous work on the electrodeposition of chromium from tervalent salt solutions reveals the conflicting nature of the observations. Most of the work appears to have been done without the aid of any guiding theoretical principles, and without due regard being paid to the complex nature of the chromium salt solutions used and to their hydrogen ion concentrations.

Whatever may be the electrolyte from which chromium is deposited, its deposition is always accompanied by the discharge of considerable amounts of hydrogen. Not only may this gas-discharge have deleterious effects on the mechanical properties of the deposited chromium (and incidentally yield a low current efficiency) but, in depleting the electrolyte of hydrogen-ions in immediate contact with the cathode, the renewal of which by electrical migration and diffusion being comparatively slow, may cause a local p_H value to be set up at which basic chromium salts begin to precipitate, and so contaminate any deposited metal. The following is an outline of the considerations which have actuated the present reinvestigation of the problem. According to Luther,[19] the Normal Electrode Potential of chromium is 0·477 volt on the hydrogen scale. Hence, if this potential is reversible, chromium will not be deposited at 18° until the cathode has acquired a potential given by

$$E_{Cr} = -0.477 + \frac{0.05\bar{8}}{3} \log [Cr^{...}].$$ Moreover, if hydrogen is liberated at

the reversible potential E_H, then if this potential is less than E_{Cr}, hydrogen alone would be discharged, which may possibly be accompanied by the precipitation of basic chromium salts. If the electrolyte were 1 Molar with respect to chromium ions, then the reversible hydrogen potential would also be that of chromium, when the p_H of the solution was 8·1. From such a solution only hydrogen would be deposited unless the hydrogen ion concentration were reduced to, and preferably below, p_H 8·1. This is, of course, an ideal case, but it indicates that suitable regulation of the p_H of the chromium salt bath is likely to lead to more successful metal deposition. With chromium salts of strong acids, the use of p_H 8·1 is impossible, for the solutions become precipit-

[18] *J. Russ. Phys. Chem.*, 2221, 1929.
[19] *Z. physikal. Chem.*, 36, 389, 1901 ; see also, Aten, *Proc. Amst. Acad.*, 20, 812, 1917-18 ; and Baumann, *Rec. Trav. Chem.*, 43, 1, 1924.

able in the region of p_H 5.[20]   Except in very few instances, the evolution of hydrogen does not occur at the theoretical potential, but takes place at a more negative value, depending among other things, on the current density and temperature employed.   Increase of current density increases this hydrogen " overvoltage," and raising the temperature, brings about a rapid lowering.   Then there is the effect on the hydrogen over- voltage of the metal upon which the chromium is to be deposited.   At low current densities, the overvoltage at a copper cathode is 0·23 volt, whilst at a nickel cathode it is 0·21 volt.[21]   Hence, for any chromium to be deposited from a molar solution, it would appear necessary for the concentration of hydrogen ions to be reduced to at least p_H 4·3.   As the overvoltage effect is increased by the use of higher current densities, it follows that it should be possible to use electrolytes of lower p_H (at higher current densities).   The following two factors will effect the precise potential at which chromium will be deposited : (i) concentration polarisation, (ii) nature of the species of tervalent chromium ions.   The former will tend to lower the deposition potential.   This will be obviated, to a large extent, by efficient stirring.   The latter is a very complex problem, and is certainly the chief cause of the conflicting results that have previously been obtained.   Despite all that has been done on chromium salt solutions, it can be safely said that the exact mode of ionisation and the nature of the chromium ions still awaits discovery. This is especially true of the basic chromium chloride and the basic chromium sulphate solutions that have been investigated in the following experiments.   The preparation of solutions at low temperatures appears to be conducive to the existence of a simpler form of chromium ions. For this reason, it was considered advisable to prepare all solutions, when possible, in the cold, and to electrolyse them at ordinary tempera- ture.   The use of higher temperatures certainly leads to the formation of more complicated ions, and therefore tends to render chromium electrodeposition more difficult.[20]

It appears that chromium deposition will be facilitated by employing an electrolyte whose chromium salt concentration is high and whose hydrogen ion concentration is as low as possible.   By analogy, however, with the nature of the deposits of silver and copper obtained from baths having high metal contents, it seems possible that a high chromium salt concentration might lead to unsatisfactory, coarsely crystalline, deposits, and that it might be necessary to use electrolytes, which, whilst having a high chromium content, possess a relatively small amount in a suitably ionised condition to give fine-grained metal deposits. It was considered that stable complexes of chromium in combination with certain organic acids might satisfy this requirement, and, at the same time, allow the use of electrolytic baths at relatively high p_H values.[22]   It is just possible that the success of the chromic acid bath is due to its having a small concentration of tervalent chromium ions, that are probably responsible for electrodeposition and a large chromium reserve as CrO_4'' ions, which through the ionic equilibrium between CrO_4'' ions and Cr''' ions maintains the bath at a suitable concentration with regard to the latter.

The work outlined in this paper deals solely with simple chromium salt solutions, and work dealing with more satisfactory electrodepositons

[20] Cf. Britton, *J. Chem. Soc.*, 2127, 1925.
[21] Cf. Caspari, *Z. physikal. Chem.*, 30, 89, 1899.
[22] *Vide* Britton, *J. Chem. Soc.*, 269, 1926.

from solutions containing chromium in the form of complexes with organic acids will be described in a later paper. This paper also contains further work that was deemed necessary on the precipitation of chromium hydroxide from solutions of concentrations typical of those used for electrolyses.

Experimental.

1. Hydrogen Ion Concentrations Prevailing during Precipitation with Sodium Hydroxide from Concentrated Solutions of Chromium Chloride and Sulphate.

In order to obtain some idea of the effect of the changes in hydrogen-ion concentration that occur in the catholyte, and particularly in the film of liquid in the immediate contact with the cathode, the following titra-
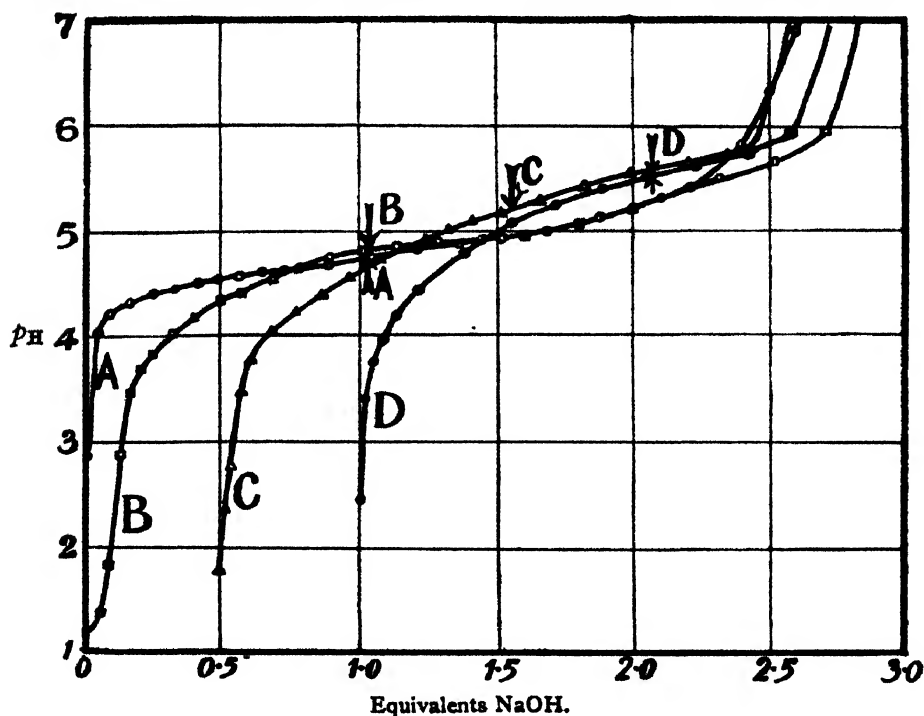
Equivalents NaOH.
FIG. 1.

tions have been made of solutions of chromium salts that were 0·5 M, with 2·0 N sodium hydroxide. The measurements were made at 18° with the quinhydrone electrode. The precipitation curves corresponding to the various chloride solutions are given in Fig. 1, whilst those obtained with sulphate solutions are shown in Fig. 2.

The chloride used was green and crystalline, and analysis showed it to be $CrCl_3$, $6H_2O$. A freshly-made 0·5 M solution has a p_H of 2·85. Its precipitation curve, A in Fig. 1, shows that the first addition of alkali cause a sudden increase in p_H to take place. After p_H 4·3, the change was gradual to p_H 4·8 when precipitation was observed to begin. This required slightly more than one equivalent of alkali. Curve B is that of a similar solution, that had been heated to boiling and then cooled before addition of alkali. As found by Britton [20] in the case of

o·oi M solutions, such treatment causes the liberation of free acid and the consequent production of a basic chromium chloride in the solution. For this reason, the sudden rise in p_H that occurred in the previous titration was deferred until somewhat more alkali had been added, but precipitation occurred at almost the same p_H as with the same amount of alkali. Curve C, Fig. 1, refers to a 0·5 M chromium chloride solution to which 0·5 equivalent of sodium hydroxide had been added, then boiled, immediately cooled and treated with alkali. By comparing the p_H corresponding to the addition of 0·5 equivalent of alkali (*viz.*, p_H 4·6) with the p_H indicated at the beginning of Curve C (*viz.*, p_H 1·8) it will be seen that boiling causes sufficient hydrolysis of the soluble basic chloride to cause a thousand-fold increase in hydrogen ion concentration.
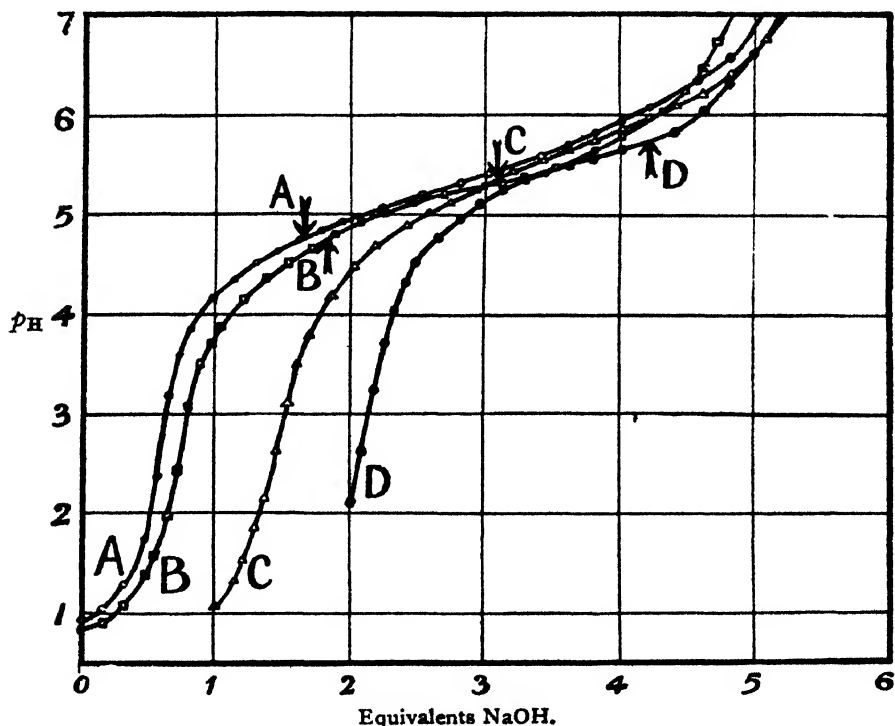
Equivalents NaOH.
FIG. 2.

The precipitation of chromium hydroxide from this solution was somewhat delayed, and began at p_H 5·2. A similar change, though not so large, occurs on allowing the basic solution stand for some time. Curve D corresponds to a solution to which one equivalent of alkali was added before boiling, cooling and titration. A similar increase in hydrogen ion concentration was produced and precipitation was delayed until the basic chloride was slightly more basic than $Cr(OH)_2Cl$ and a p_H of 5·6 was reached.

The various curves given in Fig. 2 were obtained with chromium sulphate solutions that had received the same treatment as the different chloride solutions; the respective curves being marked by the same letters. The chromium sulphate used was an ordinary commercial pseudo-crystalline product obtained from Messrs. Hopkin and Williams.

Whilst the curves are similar in shape, and give the same precipitation range of p_H as shown in Fig. 1, it will be observed that the hydrogen ion concentration of the original solution of chromium sulphate (Curve A), was considerably higher than that of the chloride. The explanation for this difference undoubtedly lies in the precise manner in which the chromium salts were prepared.

Electrolysis of Tervalent Chromium Chloride Solutions.

Electrodes.—The cathodes were of thin sheet copper, 3 cm. by 2 cm. soldered to copper wire leads. Before use, they were thoroughly cleaned and polished. Nickel cathodes used in later work, in the form of thin sheet, were also made in the same manner. Two types of anode were used : insoluble and soluble. As insoluble anodes platinum was used. They were made of thin sheet, 2 cm. by 2 cm., and were welded to platinum wire, which was sealed into glass tubes containing mercury. The provision of suitable soluble chromium anodes was a matter of some difficulty. Attempts were first made to use copper electrodes that apparently had been covered with heavy layers of electrolytic chromium that had been deposited from the usual chromic acid bath. They, however, were unsatisfactory, for in the course of electrolysis a network of fine cracks became visible and caused the underlying copper to be attacked. Unfortunately, chromium cannot be procured in the form of either rods or sheets ; that prepared by Goldschmidt process was obtained in irregular crystalline pieces. An attempt was made to use these lumps by mounting them in platinum foil. In chloride baths this type of anode was useless, for the platinum also behaved anodically and chlorine was evolved. The best way (though one that was not uniformly successful) was to fix the more suitable lumps in brass clamps, and then to cover the brass parts that were to dip in the solution with a thorough coating of paraffin wax. Another method adopted was to mount the larger lumps in a steel spring in such a way that only a part of the chromium surface was exposed to the electrolyte. Only approximate estimates could, of course, be made of the effective surface of these chromium anodes.

The Electrolytic Cell.—For this purpose a 250 c.c. beaker was used. It was filled with a mechanical glass stirrer having a speed of approximately 400 r.p.m. The vessel was immersed in a constant-level water bath, through which water could be passed at any desired temperature. The distance between the two electrodes was 4 cm. The current was obtained from a battery of eight high-capacity accumulators. In the experiments involving diaphragms porous pots having walls of 4 mm. thickness were used. The diameter of the pots was 3·5 cm. and height, 7 cm. When not in use, they were kept in running water. A voltmeter was placed across the poles of the bath and the quantity of electricity passed was measured by means of an ammeter placed in the main circuit in series with a rheostat.

The amounts of chromium actually deposited were estimated by a gasometric method used by Carveth and Moth. This consisted of measuring the volume of hydrogen evolved when the cathode was placed in a dilute solution of hydrochloric acid, it having been shown that the gas immediately liberated corresponded to the dissolution of the chromium as chromous chloride. The purity of the deposits was ascertained from the weights of chromium deposited and that of the total cathode deposits.

Experimental Results.

Part I.   Chromium Chloride Solutions.

A. Electrolysis without a Diaphragm.

(a) *The Effect of Varying Concentration and Cathode Current Density.* —Solutions of concentration 1·0, 2·0, and 3·0 Molar were electrolysed at current densities from 8·3-33·3 amp./dm². at room temperature (15-20° C.) using copper cathodes, and (i) platinum and (ii) chromium anodes.

Very poor deposits were obtained, ranging from dull grey to black, and showing very little metal. Fig. 3 (a) is a photograph of typical deposits. The left-hand column depicts deposits obtained by using a platinum anode, and those on the right hand with a chromium anode; the rows correspond to current densities of 8·3, 16·6, and 25·0 amp./dm². Efficiencies were low, all less than 5 per cent, except at 33·3 amp./dm². with the 3·0 *M* solution, which gave a value of 8·6 per cent. The values with a chromium anode were slightly lower than with platinum. Despite these poor results, there is sufficient evidence to show that increased concentration and current density tend to give better deposits.

(b) *The Effect of Temperature.*—Electrolysis was repeated at 40° and 60° C. Even poorer deposits were obtained, and consisted chiefly of brownish films or thin layers. Small areas of metal were apparent at higher concentration and *C D*, but the results were generally so poor that the efficiencies were not determined. Under the conditions of experiment, increased temperature appeared therefore not to be advantageous.

The failure to produce good metallic deposits is at variance with the results of earlier workers; thus Cowper-Coles [12] reported that good metal deposits were obtained from a solution of 25 parts of chromium chloride in 75 parts of water, using lead anodes with a cathode current of 4·5-5·5 amp./dm². and a temperature of 90° C. We have repeated electrolysis according to these directions; periods of three hours being allowed. An appreciable amount of lead chloride was formed and collected on the cathode. When removed, a slight brown film was left. Subsequent deposits were brownish-black, and the final deposit showed thin smooth dull grey metal under a heavy layer of lead chloride. No efficiencies are given by Cowper-Coles; those obtained in this work were less than 1 per cent. In order to avoid contamination of the deposit with basic matter Cowper-Coles added a little free hydrochloric acid to the electrolyte to maintain it in solution. In these experiments, it was found that such solutions yielded similar brownish black deposits on electrolysis, but at 40-50 amp./dm². a little bright metal was obtained. Using a considerable amount of hydrochloric acid, Férée [13] claims to have obtained steel grey chromium from a chromium chloride solution. This work, however, was not re-investigated.

B. Electrolysis using a Diaphragm.

(a) *Experiments using the same Solution as Anolyte and Catholyte.*— The interposition of a diaphragm gives a partial separation of anode and cathode effects; the former leads to the formation of sexavalent chromium and also dissolved chlorine. The separation of the catholyte makes it more susceptible to the changes caused by cathodic evolution of hydrogen, since the restoring effect of the bulk of the solution is

Fig. [illegible]

Fig. [illegible]

largely retarded by the diaphragm. Solutions of chromium chloride of the same concentration as above were electrolysed over the same range of current densities The quality of the deposits was distinctly better though pure metal was not obtained. Fig. 3 (*b*) is a photograph of typical deposits. Except for the diaphragm, they were deposited under similar conditions as those shown in Fig. 3 (*a*). The metal was concentrated more at the edges, and was rough and non-adherent, and the necessary handling caused the marginal deposit to become detached more so with the deposits formed at higher $C D$. Spots are noticeable in the body of the deposits showing that they were not pure through inclusion of basic matter Treatment with acid to dissolve the chromium leaves the impurity as a black film on the electrode which suggests that this impurity is deposited first, and this probably accounts for the poor mechanical properties of the deposits

Table I. below gives the cathodic efficiencies for these conditions.

TABLE I

$C D$ amp /dm².	Platinum Anode using CrCl₃ of Conc			Chromium Anode using CrCl₃ of Conc		
	1 0 M	2 0 M	3 0 M	1 0 M	2 0 M	3 0 M
8 3	0 67	1·2	3 8	0·08	0·78	2 2
16·6	1·0	5 0	9·0	2 3	6·8	7 4
25 0	1·2	10·8	12·3	2 3	12 8	15·0
33 3		5·8	6·3	–	10 0	7·5

The percentage purity of the deposits varied irregularly between 30-80, though there was a general tendency to higher purity with higher $C.D.$ An attempt was made to obtain some idea of the extent of anodic oxidation of the chromium At the end of the run a portion of the solution was freed from chlorine by boiling and then the sexavalent chromium was estimated iodimetrically As boiling may have caused further oxidation, the result must be regarded as approximate Although the variations were somewhat erratic (between 0·0-2·0 per cent.), they exhibited a tendency to increase with increasing $C D$. and to decrease with increasing concentration of the chromium chloride Oxidation at the chromium anode was almost negligible Similar experiments performed at 40° C. gave poorer deposits and slightly lower efficiencies (4·0-12·0 per cent.) Less anodic oxidation occurred

(*b*) *Using Different Anolytes.* The greater part of the earlier work in this subject was done with a foreign anolyte Glaser (*loc cit*, by using mineral acids and salts as anolytes, states that he secured good metal deposits with efficiencies of 40 per cent As high as 85 per cent efficiency is claimed, though the change of anolyte is not specified. He gives no details of his experiments, and especially of the method of determining efficiencies In view of the present authors' experiments such high values seem unlikely. Carveth and Mott [15] used various acid and salt solutions, and report values of the order of 20 per cent. with a maximum value of 50 per cent. with ammonium hydroxide at 50° C. The best $C D$ range was 10-40 amp /dm², while increased temperature

gave decreased efficiency and poorer quality deposits. In our experiments, hydrochloric acid, potassium and ammonium chlorides were used as anolytes, being the compound of the anion of the catholyte with hydrogen, a strong and a weak base respectively.

Solutions of chromium chloride, 1·0 M, 2·0 M, and 3·0 M were electrolysed as catholytes, and the above as anolytes, with platinum anodes. There is obviously no need to use soluble anodes. The hydrochloric acid was 1·0 M, the ammonium chloride 3·0 M, and the potassium chloride saturated at the temperature of the bath. In no case was pure metal deposited. With hydrochloric acid, the first run gave impure metal at low efficiency and further electrolysis resulted only in brown films of basic matter. With ammonium chloride, higher efficiencies were obtained, and although the deposits were metallic in appearance, their quality was poor. They became worse as the concentration of the catholyte was raised and also with increasing $C.D.$

TABLE II.—ANOLYTE : 3 M. AMMONIUM CHLORIDE. CATHOLYTE : CHROMIUM CHLORIDE, 1 M., 2 M., AND 3 M.

C.D. amp./dm².	1 M CrCl₃.		2 M CrCl₃.		3 M CrCl₃.	
	Efficiency.	Purity.	Efficiency.	Purity.	Efficiency.	Purity.
16·6	5·9	81·5	11·6	93·7	15·1	91·0
25·0	1·0	42·5	22·0	58·6	20·6	57·3
33·3	—	—	23·1	43·0	25·6	18·7

The deposits were grey-black of varying shades, with purer looking metal at the edges of the electrodes. Treeing was common, and caused non-adherence. Dissolution in acid left the black films that are characteristic of impure deposits. Potassium chloride gave similar deposits but lower efficiencies. Treeing was more noticeable, and the metal at the edges was more broken than with the ammonium chloride deposits. Efficiencies varied from 6·3 to 21·3 per cent., and the purity from 40 to 66 per cent.

A series of anolytes was investigated briefly. The conditions and results are indicated in Table III.

TABLE III.—CATHOLYTE : 2 M. CHROMIUM CHLORIDE. CATHODE : CU. ANODE : PT. ROOM TEMPERATURE (15–20° C. CATHODE C.D. = 16·6 AMP./DM². TIME OF ELECTROLYSIS = 30 MINUTES.

Anolyte.	First Run.		Immediate Repeat.	
	Efficiency.	Purity.	Efficiency.	Purity.
Amm. Chloride, 3·0 M.	4·3	84·9	14·1	67·8
Ammonium Sulphate Sat.	2·2	81·8	7·7	88·0
Ammonium Acetate ,,	1·8	61·2	8·7	65·1
Ammonium Oxalate ,,	1·8	92·0	1·8	74·0
Potassium Chloride ,,	4·4	95·0	27·6	78·0
Potassium Sulphate ,,	—	—	4·3	27·3
Sodium Acetate ,,	1·5	87·2	2·7	80·0
Potassium Oxalate ,,	—	—	5·2	70·6

The deposits from the first electrolysis were dark-grey to black, with the exception of those obtained with potassium sulphate and oxalate as anolyte. The latter of these was light-brown, and contained no metal, while the former was a darker brown, and showed traces of metal at the edges, since a faint hydrogen evolution occurred there when the deposit was treated with hydrochloric acid. Of the deposits obtained in the second electrolysis, that with ammonium chloride as anolyte was slight grey, the metal being loose and treed at the edges. That with potassium chloride was of similar character, the treeing at the edges being more marked. The other deposits were also of similar grey metal, but treeing was absent.

Comparison of the efficiencies obtained in the second set of experiments with those found in the first series reveals that, with one exception, viz., using ammonium oxalate, increased deposition took place from the baths on continued electrolysis, which was also the experience of Carveth and Mott. This is particularly true when either ammonium or potassium chloride was used.

C. Addition of Alkali Chlorides.

The obvious effect of the addition of alkali chlorides will be to increase the conductivity of the solutions and hence to lower the voltage across the electrodes. This should reduce the tendency to " treeing," and lead to a more even distribution of metal. Electrolysis was carried out with 1 M—chromium chloride solutions that were respectively 1, 2, and 3 M with respect to alkali chlorides, viz., either potassium or ammonium chlorides. Two series of experiments were carried out at room temperature, without and with a diaphragm, using copper cathodes and platinum anodes and $C.D.$ ranging from 10 to 50 amp./dm².

TABLE IV.

C.D.	KCl.						NH₄Cl.					
	1·0 M.		2·0 M.		3·0 M.		1·0 M.		2·0 M.		3·0 M.	
	Efficiency.	Voltage.	Efficiency.	Voltage.	Efficiency.	Voltage.	Efficiency.	Voltage.	Efficiency.	Voltage.	Efficiency.	Voltage.
20	1·5	7·2	2·7	5·1	1·4	4·7	3·6	5·6	3·6	5·4	2·8	4·7
30	6·5	9·0	7·7	6·6	8·7	6·6	11·0	7·9	7·4	6·8	16·1	6·0
40	8·7	9·8	11·4	7·4	12·7	7·2	9·1	9·0	12·0	8·1	20·4	6·9
50	10·8	11·6	12·3	8·3	15·4	7·9	—	—	12·5	9·3	16·3	7·1

(a) Without the Use of a Diaphragm.—The deposits which ranged from light-grey to dull-black had poor mechanical properties. They were loose and broken, especially at the edges, and treeing was more frequent than with simple chloride solutions. In Table IV. are given efficiencies and voltages at various current densities for the solutions. It will be observed that increase in the concentration of alkali salts caused a progressive decrease in voltage and an increase in efficiency. The effect on the quality of deposited metal was, however, indefinite. The purity was higher than with simple chloride solution, and varied from 67 to 90 per cent.

Solutions of this type have been patented by the Ternstedt Mfg. Co.,[10] and the following is given as a typical solution : 1 litre contains 300 g. of chromium chloride ($CrCl_3$, $6H_2O$), 250 g. of sodium chloride, 150 g. of ammonium chloride, 75 g. of oxalic acid, 2·5-3·5 g. of sodium fluoride. In addition, the solution contains 1 per cent. of nitric acid. The solution is to be electrolysed without a diaphragm at 27°-70° C. with a *C.D.* of 28-112 amp./dm². with a soluble anode. We attempted to realise these conditions, but it was not found possible to prepare the solution at such concentration, even when subjected to protracted boiling and also to long standing in the cold. The solution, however, was filtered, and the filtrate electrolysed with a chromium anode at 22°-42° C., using a range of *C.D.* of 20-60 amp./dm². The residue was chiefly undissolved alkali salt, and a little entrained chromium salt. The earlier runs gave thin brown deposits showing no trace of metal, while the later ones gave greyish-black metal with basic matter included. The solution was electrolysed for about four hours, with short breaks to replace the cathode. It appears that the solution was useless within the range of temperature, and *C.D.* here studied, though it is just likely that higher *C.D.*'s might have been more advantageous.

(*b*) *Using a Diaphragm.* (1) *With the same Anolyte and Catholyte.*— Interposition of a diaphragm caused little change in the type of deposit. Its purity fell off more rapidly as the quantity of current passed was increased. The final deposits with ammonium chloride solutions were green and basic. As shown by Table V. the efficiencies were higher.

TABLE V.

C.D. (amp./dm².).	1 *M* CrCl₃ + KCl of Conc.		1 *M* CrCl₃ + NH₄Cl of Conc.		
	1·0 *M*.	2·0 *M*.	1·0 *M*.	2·0 *M*.	3·0 *M*.
10	3·9	3·5	3·1	4·5	1·8
20	14·9	13·4	15·1	18·9	17·5
30	20·1	22·2	17·2	19·6	16·5

(2) *Using Different Anolytes.*—In this case 1 *M* solutions of either potassium or ammonium chloride were used as anolytes. As catholyte 1 *M* chromium chloride solution was employed that contained the same alkali chloride as was used in the anolyte. Whereas the concentration of the alkali chloride of the anolyte was kept constant, that of the catholyte was varied, as shown in Table VI. The deposits did not differ very much from those obtained in the foregoing experiments in which no diaphragm was used. The tendency to deposit green basic matter on

TABLE VI.

C.D. (amp./dm².).	1 *M* CrCl₃ + KCl (Conc.).		1 *M* CrCl₃ + NH₄Cl (Conc.).		
	2·0 *M*.	3·0 *M*.	1·0 *M*.	2·0 *M*.	3·0 *M*.
10	4·6	5·9	2·0	2·2	2·2
20	17·3	15·6	17·0	16·3	20·3
30	13·5	14·3	20·2	26·8	15·3

continued electrolysis was more pronounced. The efficiencies were also of the same order, and are recorded in Table VI.

Férée[13] reported good deposits and efficiencies up to 45 per cent., with a solution that was 1 M with respect to chromium chloride, and 3 M with respect to potassium chloride, using platinum anodes and a diaphragm. This is not confirmed by the above work, and recalculation of his data shows a true efficiency of 23 per cent.

D. Soluble Basic Chromium Chloride Solutions.

The addition of caustic soda to chromium chloride solution causes an increase in p_H, and this addition may be continued until 1 equivalent of alkali has been added without precipitation occurring. Solutions have been investigated, containing 0·25, 0·5, 0·75 and 1 equivalent of caustic soda to 1 equivalent of chromium chloride. The solutions were prepared in the cold, since p_H measurements showed that boiling causes appreciable hydrolysis of the chromium chloride. These solutions were electrolysed over a $C.D.$ range of 8·3-33·3 amp./dm². with either platinum or chromium anodes and copper cathodes at room temperature, both without, and with a diaphragm. In Tables VII. and VIII., the numerals I., II., III., IV., refer to solutions containing the above proportions of alkali in ascending order.

(a) *Without the Use of a Diaphragm.*—Fig. 4 is a photograph of deposits obtained under these conditions, and show that pure metal is still not realised. The four pairs of columns refer to solutions I.-IV. above, the left-hand column of each is obtained with a platinum anode, the other with chromium, and the rows correspond to $C.D.$'s of 8·3, 16·6 and 25·0 amp./dm². from top to bottom. Solution 1 yielded dull black deposits at the lower $C.D.$'s, while at the higher, grey metal was produced, but was heavily spotted with basic matter, and this is more noticeable when the soluble anode was used. The change with the increase in the amount of current passed is probably due to the more favourable p_H conditions set up in the neighbourhood of the cathode. Solution II. at the lowest $C.D.$, gave dull black matter, whilst by using higher $C.D.$ some metal was deposited, but it was appreciably contaminated. A further increase $C.D.$ yielded fairly smooth metal, with only a little basic matter. The increase in p_H allows of a more rapid attainment of the most suitable conditions. Further increase of p_H as in solutions III. and IV. gave the best conditions still more quickly, and continued electrolysis caused them to be followed by conditions in which the quality again deteriorated, the change being more marked with the chromium anode.

Table VII. gives efficiency and purity data for these solutions.

Repetition of these electrolyses at 40° C. gave much poorer results the deposits at the lower concentration of chromium salt being basic matter only, while the higher concentration gave some metal of poor quality and fairly heavily contaminated.

(b) *With the Use of a Diaphragm.*—In order to prevent the changes occurring in the anolyte from interfering with electrodeposition, the experiments described in the previous section were repeated by separating the anolyte and catholyte by a diaphragm, the same solutions being used on each side. Typical deposits are illustrated in Fig. 5, and were produced from solutions of the same concentrations as those shown in Fig. 4, occupying corresponding positions. It will be seen that the better deposits were obtained from solutions to which 0·5 and 07·5 equivalent (to 1 Cr) of sodium hydroxide had been added. Solutions

TABLE VII.

C.D. (amp./dm².).	Conc. CrCl₃.	Platinum Anode.				Chromium Anode.			
		I.	II.	III.	IV.	I.	II.	III.	IV.
Cathode Efficiencies.									
8·3	1·0 M.	—	—	—	—	0·7	1·2	1·3	1·4
16·6	,,	0·2	0·2	0·2	1·9	0·9	2·9	3·3	3·8
25·0	,,	0·8	2·4	3·8	4·0	1·8	4·8	4·8	3·9
33·3	,,	1·3	2·6	4·8	6·7	2·5	6·1	5·5	5·1
8·3	2·0 M.	—	1·3	1·5	5·2	—	0·6	1·5	7·3
16·6	,,	1·2	4·0	3·8	12·4	1·2	4·8	6·4	10·9
25·0	,,	1·9	5·9	9·1	14·8	2·9	4·1	10·1	12·6
33·3	,,	1·9	8·2	12·3	13·0	5·1	4·7	11·3	12·0
Purity of the Deposits.									
8·3	1·0 M.	—	—	—	—	18·3	50·0	50·0	51·0
16·6	,,	28·6	66·0	47·0	44·0	50·0	35·5	60·0	66·0
25·0	,,	66·0	72·6	90·5	91·3	42·6	—	71·5	54·6
33·3	,,	49·0	66·0	90·0	70·0	66·0	66·0	51·0	44·8
8·3	2·0 M.	—	50·0	—	43·0	—	28·5	81·0	49·0
16·6	,,	33·0	—	53·0	66·0	35·0	42·0	78·0	59·0
25·0	,,	50·0	70·0	91·0	74·0	46·0	57·0	70·0	56·0
33·3	,,	43·0	78·0	85·0	61·3	64·0	57·0	66·0	50·0

that had been rendered basic to the extent, CrCl₂OH, tend to precipitate in the course of electrolysis, and this is reflected in the much poorer deposits obtained therefrom. This is in accord with the titration curves of these solutions given in Fig. 1, as the depletion of the catholyte of hydrogen ions is analogous to the addition of free alkali, and thus brings the solution to incipient precipitation. In using the less basic

TABLE VIII.

C.D.	Conc. CrCl₃.	Platinum Anode.				Chromium Anode.			
		I.	II.	III.	IV.	I.	II.	III.	IV.
Efficiency.									
8·3	1·0 M.	4·8	5·6	4·6	4·7	1·5	4·8	3·9	3·2
16·6	,,	7·2	4·8	1·5	—	16·4	6·8	4·8	—
8·3	2·0 M.	1·1	1·5	7·2	11·6	·8	3·5	6·2	11·2
16·6	,,	11·7	13·2	15·5	14·0	11·6	12·1	21·6	15·0
25·0	,,	18·5	20·7	16·4	—	23·2	27·9	22·6	—
33·3	,,	21·0	—	—	—	24·7	—	—	—
Purity.									
8·3	1·0 M.	89·4	83·9	72·7	43·8	75·3	79·3	76·2	25·6
16·6	,,	50·9	29·0	10·5	—	83·0	43·7	19·7	—
8·3	2·0 M.	56·1	—	93·6	76·8	68·8	83·3	84·5	82·4
16·6	,,	83·1	90·0	86·8	54·7	79·0	—	79·0	69·0
25·0	,,	84·4	74·3	49·2	—	71·1	75·0	63·0	—
33·3	,,	68·1	—	—	—	65·1	—	—	—

solutions, the more suitable conditions as regards the hydrogen ion concentration of the catholyte were realised without bringing the solution too near the point of precipitation. On repeated electrolysis the chromium chloride becomes increasingly basic, and this is accompanied by the risk of contamination of the deposit with precipitated chromium hydroxide.

Table VIII. gives the efficiency and purity data for this section.

Anodic oxidation in these solutions amounted to 1·0 to 1·5 per cent. It was greater in the more basic solutions, and also when high current densities were employed. On the other hand, higher temperatures and concentrations of chromium salt tended to give lower values. The use of a chromium anode appeared to be without any appreciable effect.

Part II. Chromium Sulphate Solutions.

A. Normal Chromium Sulphate.

The investigation of chromium sulphate solutions was not so extensive, for it was believed on the basis of the results of the experiments with chromium chloride that the use of a chromium salt alone was scarcely likely to give satisfactory results.

(a) *Without a Diaphragm.*—A concentrated solution of the sulphate was prepared, and analysis showed it to be 2·35 M. It was viscous and of high resistance, so that the normal $C.D.$ range could not be followed with the apparatus at our disposal. The deposits obtained were very poor, being chiefly purplish-grey matter. Some of the deposits contained chromium for they dissolved in hydrochloric acid with the evolution of a little hydrogen and left a brown film of basic matter which could be easily wiped off. Dilution to half the concentration gave a less resistant solution, and the usual $C.D.$ range could be followed. The

TABLE IX.

Conc. $Cr_2(SO_4)_3$.	C.D.	Platinum Anode.		Chromium Anode.	
		Efficiency.	Purity.	Efficiency.	Purity.
0·59 M.	8·3	8·8	28·7	5·2	83·3
,,	16·6	12·7	69·3	8·5	—
,,	25·0	5·1	—	10·3	74·3
,,	33·3	—	—	—	—
1·2 M.	8·3	3·2	45·3	4·1	72·4
,,	16·6	6·6	61·6	16·6	81·7
,,	25·0	13·3	78·4	20·5	49·3
,,	33·3	18·0	73·5	19·2	—
2·35 M.	8·3	2·7	—	·47	50·6
,,	16·6	4·1	58·0	·94	72·3
,,	25·0	9·7	72·8	5·8	72·7
,,	33·3	10·1	—	5·9	—

deposits were of the same type as those described above.   Efficiency varied from 0·5 to 1·5 per cent., and purity from 50 to 80 per cent.

(b) *With a Diaphragm*.   (1) *Anolyte and Catholyte the Same*.—The chromium sulphate solutions given in the first column of Table IX. were electrolysed, using a diaphragm, and either chromium or platinum as anode.   As will be observed from Table IX., the diaphragm led to higher efficiencies, though there was little apparent improvement in the quality of the deposited metal.   Even when the purity of the deposit was relatively high, the metal assumed the form of coarse crystals that were badly adherent.   " Treeing " and irregular growth of nodules was more general in the deposits formed from these solutions than was the case with chromium chloride solutions.

(2) *Anolyte Varied*.—Variation of the anolyte did not result in any marked improvement in the quality.   By using 1 M chromium sulphate as catholyte, and 3 M sulphuric acid as anolyte and a platinum anode deposits were obtained which were dull violet-grey, and contained a little metal in a finely-divided form.   The efficiencies were low (1 to 2 per cent.).   Substituting a solution of 3 M ammonium sulphate for that of sulphuric acid, similar deposits were obtained in the first two or three runs.   On continued electrolysis at 20 to 30 amp./dm^2., however, more metal, though still unsatisfactory, was obtained.   The cathodic efficiencies ranged from 5·2 to 16·7 per cent.   The ammonium sulphate in diffusing through the diaphragm caused precipitation of ammonium chrome alum on the inner walls.   This increased the electrical resistance and a fresh diaphragm was necessary.   Ammonium acetate and oxalate gave comparable results, with efficiencies of 3·0 to 14 per cent. over the same *C.D.* range.   Towards the end in each case, hydroxide matter was produced, of a fine green appearance, characteristic of that produced when excess oxalate or acetate is added to a chromium salt solution. Boiled solutions gave similar deposits, but at lower efficiencies.

B. Soluble Basic Chromium Sulphate Solutions.

As the curves given in Fig. 2, showing the effect of adding alkali to chromium sulphate solutions, are very similar to those in Fig. 1, corresponding to chromium chloride solutions, it was considered that the deposits obtained from basic sulphate solutions would bear a close resemblance to those from basic chloride solutions.   This view was supported by the electrolyses that have been performed.   The change that occurs in basic chromium sulphate solutions on boiling seemed to have an important influence on the amount of chromium that could be deposited.   Efficiencies up to 22·0 were obtained whilst unboiled solutions gave efficiencies of only 2 to 3 per cent.   It might be mentioned here that this increase was not observed with boiled basic chromium chloride solutions, probably in some way connected with the greater stability of basic sulphate complexes in solution.   None of the deposits was satisfactory as they were always impure, usually " treed " and non-adherent. Slightly higher efficiencies were obtained by interposing a diaphragm, but no improvement in the nature of the deposits was observed.   In view of the stability of basic sulphate complexes produced by reducing chromic acid with sulphur dioxide, solutions were thus prepared and subjected to similar study.   Again unsatisfactory deposits were obtained.

Discussion.

The chief aim of this work has been to ascertain the conditions under which it is possible to deposit pure chromium that has satisfactory mechanical properties, *i.e.*, fine-grained, smooth, adherent metal. Unless crystals of metal can be formed without enclosing basic matter, it is obvious that a good deposit cannot be obtained. None of the conditions employed in the foregoing experiments yielded such deposits. Their purity varied somewhat irregularly over a wide range, and even when the purities were high, the mechanical properties were poor. This was doubtless due to the large crystals formed through the use of comparatively high concentrations of tervalent chromium ions. The behaviour of these solutions when the hydrogen-ion concentration was varied, as in the experiments in which basic solutions were employed, shows that contamination of the deposits is likely to occur in such unbuffered solutions, since the evolution of hydrogen at the cathode tends to raise the p_H to the stage at which precipitation of basic matter becomes possible. The effect of increased p_H is, however, in fair accord with the theoretical considerations that the higher the p_H, the greater would be the possibility of chromium deposition, and at the same time the greater would be the risk of precipitating basic matter on the cathode. These two conditions should cause a transition in the character of the deposits, and therefore a transient set of conditions under which relatively pure metal can be deposited, and this seems to be borne out by the efficiency and purity data recorded in this paper. Time of electrolysis is an important factor, evidently due to the fact that the quantity of current passed governs the change in hydrogen-ion concentration in the vicinity of the cathode.

The results of these experiments are at variance with those of earlier workers in several cases. Carveth and Mott record much higher values of efficiency of chromium deposition from solutions of the type that we have investigated, and apparently they assumed that the deposits were as a rule pure metal. Although the portion of their work which we have repeated is in qualitative agreement as regards the variation in efficiency with time, the actual values were lower in our experiments and the quality of the deposited metal was poor. Carveth and Mott make only brief reference to the quality of the deposits, which they described as good, except those that were obtained at the end of a series of electrolyses. It has occasionally been found that an apparently good metal deposit has been superposed on an initial deposit that was contaminated with basic matter, for on dissolving away the chromium with acid, films of basic matter were found to remain on the cathode. Basic sulphate solutions were fairly completely investigated by Pampfilov and Fillipitschev, though without reference to the hydrogen-ion concentrations of the solutions. They varied the basic nature by graded addition of sulphuric acid to a solution of 40 per cent. basic chromium sulphate. Their procedure was similar to that of Carveth and Mott, but the efficiencies that they obtained were of the order of 20 to 30 per cent. From the account of the deposits it appears that they were rarely composed of pure metal.

The variation in p_H has an important effect on the quality of the deposits, but in these unbuffered solutions the best conditions for the production of good metal cannot be maintained, for they are fairly rapidly changed by the effects of electrolysis. Furthermore, presumably

the high concentration of tervalent chromium ions leads to the deposition of metal of comparatively large crystal structure that is consequently of inferior quality and value.   In general, it may be concluded that the solutions studied in this work are unsuitable as a basis for a process for the electrodeposition of chromium.

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REVIEWS OF BOOKS.

Recent Advances in Physical Chemistry.   By S. GLASSTONE, Ph.D., D.Sc., F.I.C.   (London, J. and A. Churchill, 1931.   Pp. vii + 470, with 32 figures : price 15s. net.)

During the last ten years many branches of physical chemistry have been considerably extended.   The publications dealing with these advances are dispersed through a number of journals, some in foreign languages, and no elementary connected account summarising their contents and suitable for students of chemistry has appeared.   Dr. Glasstone has made an attempt to supply a want which all teachers have felt when wishing to recommend a book which could supplement the lecture courses in the subject, and would also include references to publications which students might read.   The contents of his book comprise chapters on the electronic theory of valency, the parachor, dipole moments, molecular spectra, homogeneous gas reactions, photochemical reactions, the properties of surfaces, heterogeneous catalysis, solubility, strong electrolytes and acid-base catalysis.   Recent advances are, therefore, well covered and the choice of subjects is undoubtedly a good one.   The treatment is on the whole uniform and well balanced and the chapters are self-contained.   The mathematical knowledge assumed is within the capacity of honours students of chemistry.   In some cases, in fact, a little more might with advantage have been attempted in this direction. Although the mere statement of the formula and some examples of its application will provide the weaker student with something he can reproduce, the better student will probably turn up the references given and will, in many cases, be discouraged, since the mathematical methods used in them are much more detailed than is necessary in understanding the simpler cases in which he is interested. This applies, for example, to the use of the Poisson-Boltzmann equation in the theory of strong electrolytes, and the deduction of the equation for the orientation polarisation in the theory of dipoles.   It is possible to give the deductions in both these cases in a form intelligible to the average student, and in this way some approach to a real understanding of the problems can be made, instead of mere jugglery with unintelligible formulæ.   The same applies to other subjects dealt with, and it may be that Dr. Glasstone would have done better to have omitted some of the rather speculative ballast such as that on pages 35-39, some of the organic chemistry in Chapters I. and II., and some other material which, in any case, requires no particular mental effort for its assimilation and could have been understood in the original articles ; some of these, in fact, go no further than the

summary given in the book. The chapter on photochemistry is weaker than the rest of the book ; the mere reproduction of possible schemes of reaction mechanism, some of which are probably already out of date, without any reference to reaction kinetics, is of doubtful value. Some parts of the last chapter, also, are rather specialised and not of much general interest, and could well have been omitted to make room for more vital matters. The book is, on the whole, a very successful one and this is all the more praiseworthy in that it is the first of its kind. There is no doubt that it will prove deservedly popular with students, who will find it stimulating and a real help in their studies. The printing and illustrations are excellent.   J. R. P.

Alkalien und Erdalkalien in Ausgewählten Kapiteln. By Dr. BRUNO WAESER. (Technische Fortschrittsberichte : Fortschritte der chem. Technologie in Einzeldarstellungen. Herausgegeben von Professor B. Rassow. Band. XXVI. Dresden and Leipzig, Verlag von Theodor Steinkopf, 1931. Pp. viii + 196. Price 13.50 RM, or bound 15 RM.)

Dr. Waeser, who is known as the author of other valuable technical monographs, has summarised the recent advances in the technology of the alkalies, including the important salts of the common alkali metals, lithium, rubidium, and caesium, and of the alkaline earths, including bleaching powder and beryllium. In connection with lithium, it is stated that this metal now has a large production in Germany for alloys with aluminium and lead, very small quantities of it conferring great hardness. Beryllium is used for the windows of X-ray tubes and in alloys (beryllium bronzes). The book contains a surprising amount of well-digested information in small compass, and is not a mere summary of abstracts, since details of processes, statistics, and copious references to large works of reference and to the periodical literature and patents of Europe and America are included. Electrochemical processes are considered in some detail. There are good author and subject indexes. Dr. Waeser's monograph will be found extremely useful in surveying the recent literature and will save a great amount of time and effort in tracing information on the subjects with which it deals.

                                                                    J. R. P.

Comprehensive Treatise on Inorganic and Theoretical Chemistry. By J. W. MELLOR, D.Sc., F.R.S. Volume XI. Te, Cr, Mo, W. (London : Longmans, Green & Co. Ltd., 1931. Pp. xii + 909. £3 3s. net.)

In this volume chromium occupies 362 pages, tungsten 202, molybdenum 199, and tellurium 121. Chromium is an element of outstanding interest and importance both from a technical and a scientific point of view, and it still forms the focus of an enormous amount of research work of every kind. Much of its scientific interest arises from its extraordinary power of forming complex salts, and this element would have occupied considerably more space had all these bodies been even briefly described. There is indeed much in the author's remark that the hydrated chromium chlorides are perhaps the most peculiar hydrated salts in inorganic chemistry. In this connection it is interesting to recall that Bunsen suggested that the green and violet chromium compounds were derived from two allotropes of the metal. The physical chemistry of chromium also provides many problems for study, *e.g.* passivity, electrodeposition, the condition of chromic acid in solution, etc.

It is stated that tellurium is beginning to acquire some technical importance. Of recent years much of the purely chemical work on this element has been in connection with its carbon compounds. Perhaps this fact may be advanced as an excuse that in this, an " inorganic," work the topic of its valency is poorly treated.

There is no mention of the work of Drew, who showed that Vernon's two dimethyl telluronium diiodides are not stereoisomers.

The chemistry, both of molybdenum and tungsten is exceedingly complicated and almost as much space is needed for this as for that of more familiar metals such as tin and aluminium. Molybdenum is destined to be of considerable metallurgical importance, whilst tungsten "has arrived." Much of the modern work on these two elements is on the physical and physical-chemical aspects, and there is much room for investigations of a purely chemical nature.

Dr. Mellor has, with his usual skill, successfully brought together a mass of material which must have been very difficult to handle.

<div align="right">C. H. S.</div>

Grundbegriffe der Chemie. By Dr. E. Rabinowitsch. (Sammlung Göschen.) Pp. 151 with two illustrations. Walter de Gruyter, Berlin and Leipzig. 1930. Price 1·80 marks.

It is remarkable how much information is packed into each of the little books of the "Sammlung Göschen," and this member of the series is no exception to the rule. It would be an admirable guide for revision work in Universities, in that it comprises a quite readable account of most of the subjects dealt with in theoretical and physical chemistry.

Two points strike one as a trifle odd in a booklet otherwise so carefully balanced. The first is that, although Werner's conception of co-ordination is thoroughly discussed, no attempt whatever is made to extend it to crystallo-chemistry, in which, as Goldschmidt has stressed, it is fundamental. The second matter, important perhaps more from the philosophical than from the every-day aspect, is the habit of distinguishing between physical and chemical molecular theory. The time has surely passed for this to be profitable : efforts are directed from both sides towards unification. There cannot be one kind of molecule for the chemist, and another kind for the physicist.

Taken altogether, this small volume is an excellent production, and many memories should be refreshed by reading it from cover to cover.

<div align="right">F. I. G. R.</div>

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